Researches on Camphor, Borneol and Their Allied Substances (*Continued*).

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I. Catalytic Oxidation of Borneol and Isoborneol. Borneol (m.p. 204.2°C, $[\alpha]_D^{16°}$ +21.34 in alcoholic solution) was prepared by the reduction of camphor.

Isoborneol (m.p. 208°C in a sealed tube, $[\alpha]_D^{16°}$ −1.3 in alcoholic solution) was synthesised by the hydration of camphene, and recrystallised for several times from its solution in petroleum ether. Reduced copper which was used as catalyser was prepared by the method described by Mr. Masumoto,[28] and reduced nickel was prepared by Sabatier's method by first igniting nickel nitrate and then reducing the nickel oxide thus obtained at 300°C.

As the experimental apparatus, combustion furnace of common type was used, and camphor of the reaction product was estimated by the semicarbazone process,[29] and borneol and isoborneol by ester value after acetylation under the following conditions. During the acetylation, as the camphene itself is esterified by 13%, the content of borneol and isoborneol underwent some adjustments accordingly.

(1) borneol

Number	Weight (g.)	Saponification hours	Ester value after acetylation	isoberneol
1	2	2	266.4	93.3 %
2	1	4	283	99.1

(2) isoborneol

Number	Weight (g.)	Saponification hours	Ester value after acetylation	isoborneol
1	1	5	283	99.1 %

(1) Catalytic oxidation of borneol by reduced copper.

Catalyser	Borneol (g.)	Reaction temp. °C	Reaction time	Reaction products		
				Yield (g.)	M.p.	$[\alpha]_D^{14}$
Cu (1)	11.9	400	h. min. 2 07	11.7	177.8–178.1	+41.8
Cu (2)	11.9	400	1 55	11.6	161–163.5	+40.8
Cu (3)	11.5	400	1 55	11.1	178.8–182	+40.3

(28) Loc. cit.

(29) Yamada, *J. Chem. Soc. Japan*, **48** (1927), 341.

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(1)—*Concluded.*

Catalyser	Reaction products				
	Camphor (%)	Borneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
Cu (1)	96.3	3.5	0.2	99.8	0.2
Cu (2)	57	29	14	80	20
Cu (3)	58	33	9	87	13

(2) Catalytic oxidation of isoborneol by reduced copper.

Catalyser	Isoborneol (g.)	Reaction temp. °C	Reaction time h. min.	Reaction products		
				Yield (g.)	M.p.	$[\alpha]_D^{12}$
Cu (1)	11.2	150	2 05	10.7	166–171.8	±0
Cu (1)	9.3	300	2 00	8.2	165.5–169.1	±0
Cu (2)	10.5	150	2 15	9.6	204.4–207.9	±0
Cu (2)	10.1	300	1 55	8.1	72.5– 84.0	±0

Catalyser	Reaction products				
	Camphor (%)	Isoborneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
Cu (1)	56	37	7	89	11
Cu (1)	86	10	4	96	4
Cu (2)	0	96	4	0	100
Cu (2)	22	9	69	24	76

(3) Catalytic oxidation of borneol by reduced nickel.

No.	Borneol (g.)	React. temp. °C	React. time (hr.) h. min.	Reaction products							
				Yield (g.)	M.p.	$[\alpha]_D^{16}$	Camphor (%)	Borneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
1	10.6	200	3 25	10.1	177–178.3	+43.1	86	8	6	94	6
2	8.7	300	2 20	8.0	174.2–175.9	+42.5	90	7	3	97	3
3	11.9	400	1 30	11.6	176.5–178.8	+41.3	82	13	5	95	5

(4) Catalytic oxidation of isoborneol by reduced nickel.

No.	Isoborneol (g.)	React. temp. °C	React. time (hr.) h. min.	Reaction products							
				Yield (g.)	M.p.	$[\alpha]_D^{13}$	Camphor (%)	Isoborneol (%)	Camphene (%)	Camphor (%)	Camphene (%)
1	11.8	200	3 40	11.1	173.5–175.3	±0	81	19	0	100	0
2	12.1	300	2 40	11.1	167–168.8	±0	89	7	4	96	4
3	10.7	400	1 50	10.2	168.5–171.3	±0	75	16	9	89	11

II. Catalytic Reduction and Rearrangement of Camphor, Borneol and Isoborneol under High Pressures and High Temperatures.

Camphor—Refined camphor manufactured by the Nippon Camphor Company; m.p. 176.4°C, $[\alpha]_D^{24}$+44.13.

Borneol—By reducing the purified camphor with metallic sodium and alcohol, some borneol was obtained, which, according to the writer's own method,[30] was treated with 2 moles of phthalic anhydride under 140–145°C for 20 hours and then immediately by steam distillation volatile substances were distilled off and the residue was treated with some warm water to remove the excess of phthalic acid. The ester was purified by recrystallisation; m.p. 158–159°C, $[\alpha]_D^{11}$+52.41 (C=4 in alcohol).[31] The ester was saponified and the borneol thus obtained was recrystallised from its solution in petroleum ether; m.p. 204–204.5°C (in sealed tube), $[\alpha]_D^{15}$+38.44 (C=3.92 in toluene).

Isoborneol—Some camphor was dissolved in absolute alcohol and then was reduced by the catalytic reaction of reduced nickel under high temperature and pressure. To the isoborneol thus obtained, 2 moles of phthalic anhydride and some toluene were added, esterified by heating at 110°C for 5 hours, distilled out the volatile matter with steam, and to the residue warm water was added to remove the excess of phthalic acid. Borneol ester which contaminated the product was, as it is easily saponifiable, taken away by hydrolysis,[32] and the ester was recrystallised from its alcoholic solution, m.p. 168–168.2°C, $[\alpha]_D^{18}$ −83.07 (C=3.7 in alcohol),[33] isoborneol obtained by saponifying the ester was recrystallised from petroleum ether, m.p. 212–213°C., $[\alpha]_D$−34.42 (C=3.35 in alcohol) $[\alpha]_D^{15}$−19.59 (C=5.17 in toluene).

Nickel—Nickel nitrate was ignited to produce nickel oxide, which was reduced with hydrogen at 300°C.

The reaction product was separated from nickel, camphor was quantitatively estimated by the semicarbazone process, and borneol and isoborneol were calculated from the specific rotation of their respective solutions in alcohol and toluene, the mean number being adopted.

In cases of samples 5–9, among the reaction products some water was present, which clearly indicated that dehydration had occurred. Therefore, after the estimation of camphor, the sample was distilled over sodium and isocamphane[34] (b.p. 164.5–165°C, m.p. 66–67°C, $[\alpha]_D \pm 0$) was obtained. Found: C, 86.60; H, 13.22. Calculated for $C_{10}H_{18}$: C, 86.86; H, 13.14%.

With regard to sample 17 and 18, to prove the presence of borneol 2 moles of phthalic anhydride were added in each case and the mixture was heated to 140~145°C. for 20 hours. Thus all of the isoborneol was converted to camphene, and borneol was separated in the form of phthalic ester.

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(30) *J. Chem. Soc. Japan*, **53** (1932), 807.
(31) Pickard and Littlebury, *J. Chem. Soc.*, **91**, 1978.
(32) Vavon and Peignier, *Bull. soc. chim.*, **39** (1926), 924.
(33) Kenyon and Picard, *J. Chem. Soc.*, **107**, 59.
(34) P. Lipp, *Ann.*, **382** (1911), 279; Komatsu and Masumoto, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **5** (1922), 225.

No.	Sample	(g.)	Initial press. (atm.)	React. temp. °C.	Temp. at the beginning of absorp. °C.	React. time (hr.)	H_2 absorbed (mol.)
1	camphor	50	23.3	170~190	170	$7^1/_2$	1.1
2	camphor	50	49.4	170~200	150	$6^1/_3$	1.0
3	camphor	50	84.5	170~190	140	$5^5/_6$	1.0
4	camphor	50	79.5	140~160	150	$20^1/_2$	0.7
5	camphor	50	91.6	200~280	—	$8^5/_6$	2.0
6	camphor	50	51	190~220	160	3	1.5
7	borneol	25	49.5	130~250	210	$7^1/_2$	1.0
8	isoborneol	15	67	170~190	—	15	0.7
9	borneol isoborneol	25 25	50.5	120~256	150 220	16	1.1
10	camphor	50	55.5	170~190	150	21	1.0
11	camphor cyclohexane	50 60	78.2	140~170	—	$7^1/_2$	1.4
12	camphor abs. alcohol	50 60	90.7	140~160	130	$5^1/_2$	1.4
13	camphor acetic acid	50 0.5	61.8	170~200	—	8	1.0
14	camphor pyridine	50 0.5	85.4	180~200	—	$8^1/_2$	0.7
15	camphor cyclohexane metallic Na	50 60 1	58.2	160~170	150	$9^1/_2$	1.2

No.	Reaction product					
	Yield (g.)	M.p. °C.	$[\alpha]_D$* at °C	Camphor %	Borneol %	Isoborneol %
1	49.0	195—196	$+11.2^{20}$	20.0	51	49
2	48.0	190—194	$+10.6^{24}$	20.0	50	50
3	49.3	187—191	$+4.8^{32}$	12.0	47	53
4	48.5	194—195	$+12.1^{32}$	21.5	51	49
5	40.5 H_2O1.6	80—103	± 0	7.0	—	—
6	48.0 H_2O	119—125	$+8.3^{13}$	5.0	—	—
7	12.0 H_2O	100—110	$+3.7^{20}$	—	—	—
8	7.0 H_2O	78—79	-0.7^{10}	—	—	—
9	25.0 H_2O	78—81	± 0	—	—	—
10	49.0	197—198	$+11.8^{26}$	23.0	50	50
11	48.0	203—204	-8.2^{11}	21.0	23	77
12	47.2	208—210	-24.7^{14}	2.5	12	88
13	48.5	196—198	$+1.6^{23}$	21.5	37	63
14	49.0	199—200	$+5.5^{14}$	32.0	36	64
15	49.0	206	-7.4^{22}	8.0	33	67

* determined in alcohol.

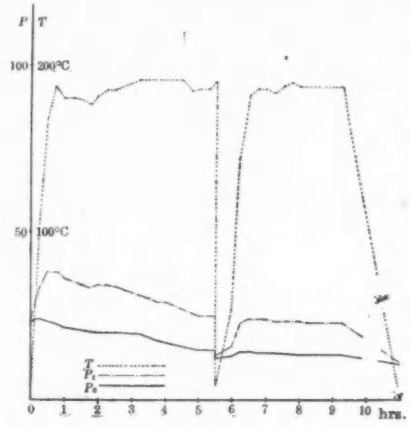
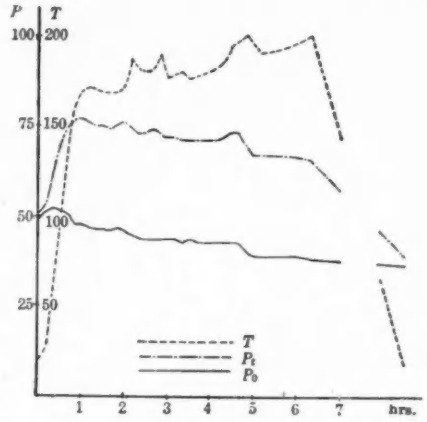


Fig. 1.



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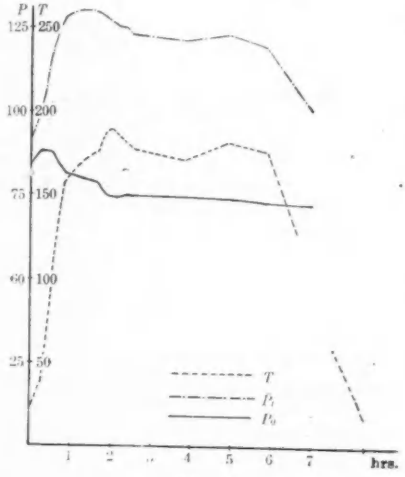

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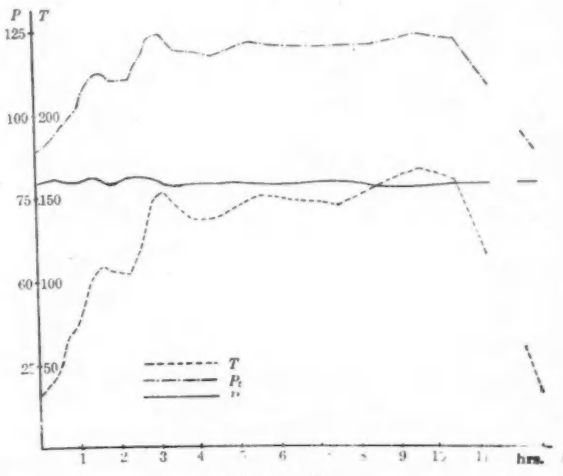


Fig. 4. (1)

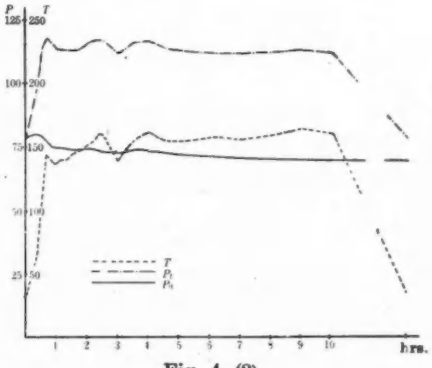
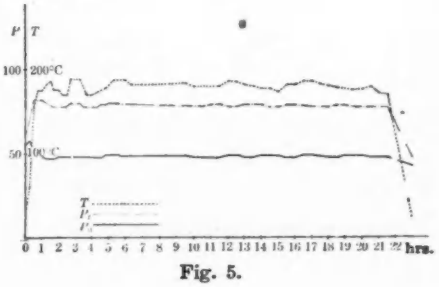


Fig. 4. (2)



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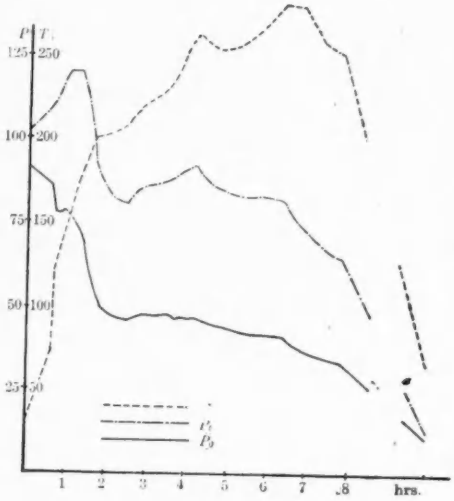

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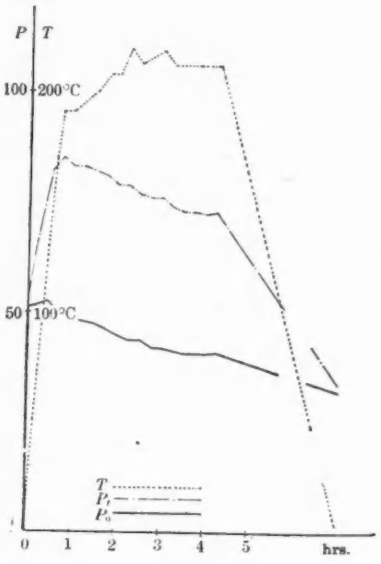


Fig. 7.

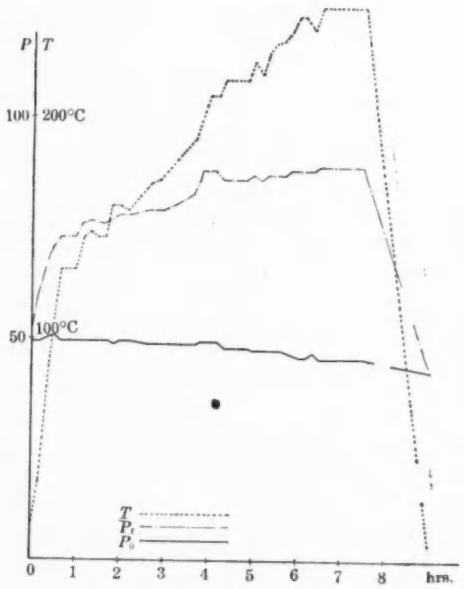


Fig. 8. Dehydration of Borneol.

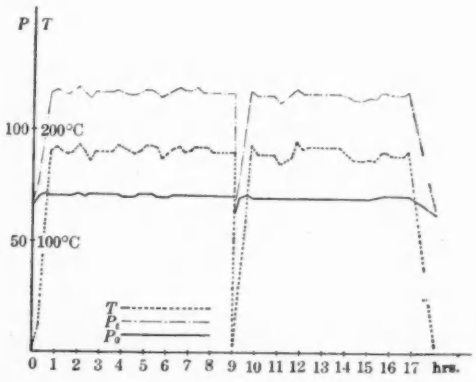


Fig. 9. Dehydration of Isoborneol.

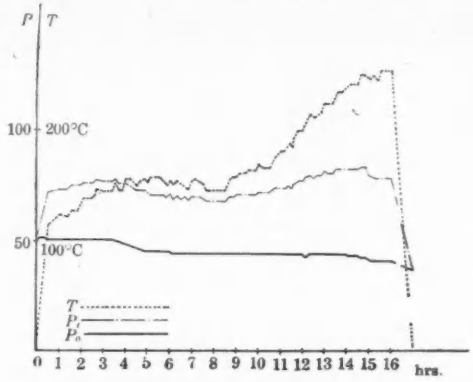


Fig. 10. Dehydration of Mixture of Borneol and Isoborneol.

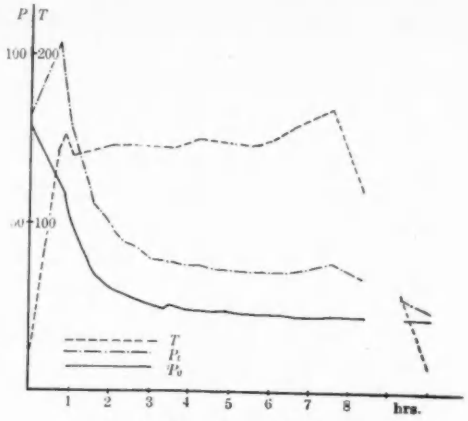


Fig. 11. Camphor+Cyclohexane.

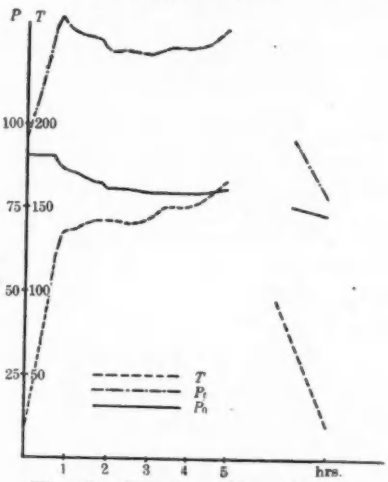


Fig. 12. Camphor+Abso. Alcohol.

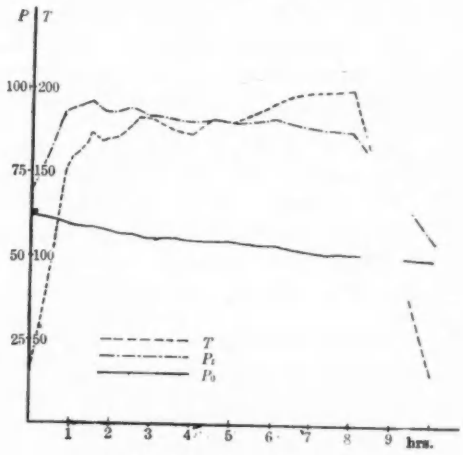


Fig. 13. Camphor+Acetic acid.

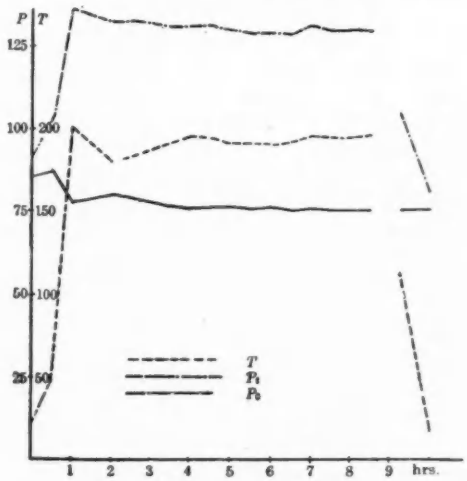


Fig. 14. Camphor+Pyridine.

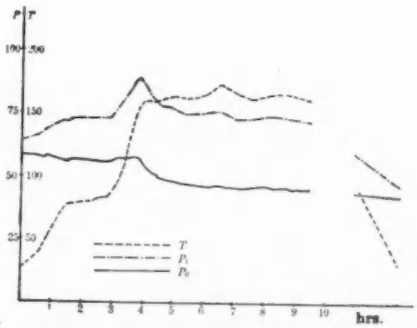


Fig. 15. Camphor+Cyclohexane+Na.

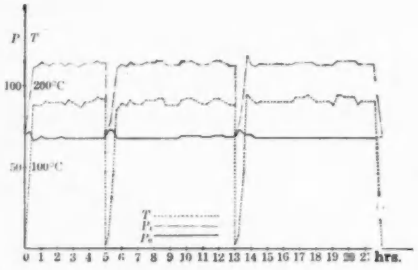


Fig. 16. Borneol.

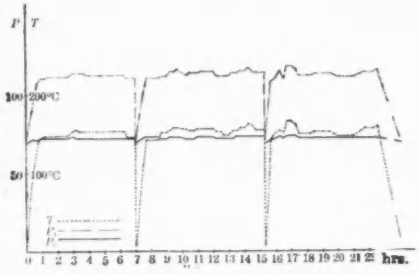


Fig. 17. Borneol-Abs. alcohol.

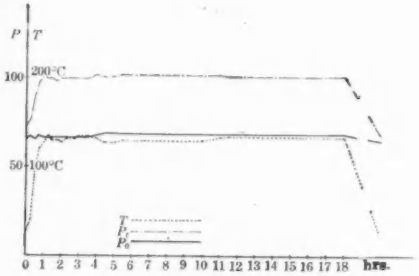


Fig. 18. Isoborneol-Abs. alcohol.

No.	Sample	(g.)	Initial press. (atm.)	React. temp. (°C)	React. time (hrs.)	H_2 absorbed (mol)
16	borneol	15	71	170—190	19.5	0.3
17	isoborneol	25	53	130—150	4	0
18	isoborneol	35	47	140—165	4	0
19	borneol alcohol	15 20	70	150—160	20.5	0
20	isoborneol alcohol	15 20	66	130—140	16.3	0.3

No.	Reaction product							
	Yield (g.)	M.p. °C	$[\alpha]_D$ alc. °C	$[\alpha]_D$ toluene °C	Methoxy value after ether. by $HCl+CH_3OH$	Camphor %	Borneol %	Isoborneol %
16	13	201—202	$+37.1^{10}$	$+38.0^{13}$	0.5	0.6	99	1
17	23	198—202	-22.2^{16}	-10.3^{16}	10.1	0.6	16	84
18	30	199—200	$+6.1^{33}$	$+10.1^{33}$		0.5	51	49
19	13	199—199.5	$+31.2^{20}$	$+33.7^{13}$	1.5	0.2	90	10
20	13.5	209—210	-25.9^{31}	-12.6^{31}	10.3	0.6	11	89

Esters	M.p. °C	$[\alpha]_D$	Borneol obtained by saponification	
			M.p. °C	$[\alpha]_D$
Acidic ester	153.5—159	+33.89	203—204	+29.68
Neutral ester	99—100	+25.05	201—202	+11.94

The esters and borneol were confirmed to be pure by the mixed fusion method. In one half of sample 19, for the purpose of proving the presence of isoborneol, it was tried to separate it as a Mg salt of phthalic acid ester, but due to the scarcity of sample, the experiment was not successful. The other half was dehydrated with phthalic anhydride and successfully confirmed as camphene. In sample 20, borneol was separated in the form of acidic ester of phthalic acid (m.p. 158–159°C.), as before. The borneol obtained by saponification; m.p. 201–202°C., $[\alpha]_D$+14.52.

III. Reduction of Dimethylcamphor with Metallic Sodium and Alcohol. (1) *α,α'-Dimethylcamphor.* According to the method of Haller,[35] by treating camphor with $NaNH_2$ and ICH_3 monomethylcamphor was obtained quantitatively. Moreover, this monomethylcamphor was repeatedly methylated; to remove the remaining camphor and monomethylcamphor, they were changed into oximes by heating at 100°C for 49 hours with 2 moles of $NH_2OH.ZnCl_2$ and after fractionally distilling 8 times, pure dimethylcamphor [b.p. 85–85.5°/8 mm, d_4^{25} 0.9460, n_D^{25} 1.4725, $[\alpha]_D^{25}$ +91.27, M.R. (obs.) 53.25, (calc.) 53.23] was obtained in a yield of 63%. Found: C, 79.86; H, 11.31. Calculated for $C_{12}H_{20}O$: C, 80.00; H, 11.11%.

(2) *Dimethylborneol.* Dimethylcamphor was reduced with metallic sodium and alcohol, and a crystalline matter (d_4^{25} 0.954, n_D^{25} 1.481, $[\alpha]_D^{25}$+46 in alcohol) mixed with oily substance was obtained 96.5%.

This reaction product was separated into 75% crystal and 25% oil; by recrystallising the crystal with petroleum ether for several times, a white needle crystal of borneol-like odour was obtained, b.p. 90.5–93°/5 mm., m.p. 57°C, $[\alpha]_D^{25}$+50.72 (C=2.11 in alcohol), $[\alpha]_D^{25}$+53.76 (C=1.71 in toluene). Found: C, 78.83; H, 12.15. Calculated for $C_{12}H_{22}O$; C, 79.12; H, 12.09%.

This substance makes a beautiful white short needle crystal of phenylurethane (m.p. 112–113°C.), and, by reacting with p-nitrobenzoic acid, forms a needle crystal of silky lustre and of faintly greenish white colour. This crystal (m.p. 115–115.8C. $[\alpha]_D^{25}$+50.94 (C=0.53 in alcohol) or +70.78 (C=0.367 in chloroform) is soluble in ether, petroleum ether, or warm alcohol, but sparingly soluble in cold alcohol. Further, it reacts with phthalic anhydride and forms monoester quantitatively.

Sample (g.)	Phthalic anhydride (moles)	React. temp. °C	React. time (hrs)	Monoester	
				Yield (g.)	%
4	2	110—115	10	7.2	99.4
5	2	140—145	20	9.1	99.6

(35) *Compt. rend.*, **148** (1909), 1645.

The moncester crystallises in beautiful white needles (m.p. 177–178°C., $[\alpha]_D^{27}$+16.32 (C=0.42 in alcohol), $[\alpha]_D^{19}$+19.12 (C=0.471 in chloroform)), and is soluble in ether, alcohol, or chloroform, but insoluble in petroleum ether and water.

The Mg salt of phthalic acid ester is white lustrous crystals of scale shape, the m.p. being 175–176.2°C. The solution of dimethylborneol in benzene was boiled with zinc chloride for 3 hours, and yet no change occurred.[36]

(3) *Dimethylisoborneol.* The oily matter (d_4^{25} 0.953, n_D^{25} 1.485, $[\alpha]_D^{29}$ +38 in alcohol) separated from the crystal already mentioned was fractionally distilled under a reduced pressure, and the following three fractions were obtained.

Fraction	B.p. 5mm	Yield (%)	d_4^{25}	n_D^{25}	$[\alpha]_D^{27}$ in alc.
1	81–87	10.6	0.9422	1.4780	+48.5
2	87–95	13.4	0.9483	1.4809	+52.3
3	95–103	71.2	0.9522	1.4831	+52.4

Each fraction was cooled with common salt and ice; from fractions (1) and (2) no crystal was obtained, and fraction (3) solidified entirely. Further, when the fraction (2) was treated with phthalic anhydride at 140–145°C. for 10 hours, unsaturated hydrocarbon was obtained as well as ester. From this experimental fact, the presence of an isomer to be easily dehydrated was suspected. Then it was tried in vain to obtain this isomer as *p*-nitrobenzoic ester by fractional crystallization. The isomer was treated with phthalic anhydride at 110–115°C. for 10 hours, the monoester thus obtained being changed to a Mg salt. Utilising the difference in the solubility in alcohol, an easily soluble crystalline powder (m.p. 180–182°C.) was obtained abundantly. This was further changed to an acidic ester, and recrystallising it from its solution in acetic acid, a lustrous beautiful crystal of scale shape (m.p. 173–174°C.) was obtained. By saponifying it, a compound $C_{12}H_{22}O$ to be considered as dimethylisoborneol was obtained, b.p. 82–84°/3 mm, m.p. 47–49°C, $d_4^{49.5}$ 0.9406, $n_D^{49.5}$ 1.4748, M.R. (obs.) 54.5, (calc.) 54.8, $[\alpha]_D^{15}$+36.47 (C=1.70 in alcohol), $[\alpha]_D^{15}$ +42.71 (C=1.43 in toluene). Found: C, 78.79; H, 12.06. Calculated for $C_{12}H_{22}O$: C, 79.12; H, 12.09%.

Phenylurethane is a lustrous, colourless needle crystal (m.p. 116–117°C.), and *p*-nitrobenzoic ester is also a lustrous, colourless needle crystal, but its m.p. is 114.5–115°C and $[\alpha]_D^{19}$+24.90 (C=0.321 in alcohol), $[\alpha]_D^{19}$+44.11 (C=0.317 in chloroform). When heated with 2 moles of phthalic anhydride at 110–115°C. for 10 hours, monoester is obtained in yield of 90%, and when the temperature was raised to 140–145°C. and

(36) Piccard and Littlebury, *J. Chem. Soc.*, **91**, 1977; Tetsusaku-Ikeda, *Proc. Sci. Inst. Japan*, **7**, 257.

the reaction was continued for about 10 hours, dehydration was complete and no ester was formed at all. And by the reaction with zinc chloride dehydration occurs.

Further, to find out the proportion of dimethylborneol and dimethylisoborneol in the reduction product which was obtained by reducing dimethylcamphor with metallic sodium and alcohol, 2 moles of phthalic anhydride was added, and, after the reaction at 110–115°C. for 10 hours, there were obtained 93% ester and 4% unesterified oil. The alcoholic part separated from the ester was again treated with phthalic anhydride at 140–145°C., and the product was separated into a substance (90%) to be considered as dimethylborneol and another (10%) to be considered as dimethylisoborneol. Unesterified oil, as it forms no phenylurethane by all means, was assumed to be a mixture of unsaturated hydrocarbons formed by dehydrating dimethylisoborneol and dimethylcamphor, and, from the bromine absorption,[37] the content of unsaturated hydrocarbons in the unesterified oil was found to be 34%.

Sample (g.)	1/5 N Br_2 sol. (c.c.)	React. time (hors)	$Na_2S_2O_3$ c.c.			Unsatur. hydrocarbon (%)
			Total Br absorbed	Br substituted	Br added	
0.2050	15	8	9.5	4.2	5.3	34.2
0.1649	15	8	7.7	3.4	4.3	34.8

As a result, the proportion of dimethylborneol and dimethylisoborneol formed was calculated to be 88:12.

IV. Catalytic Reduction of Dimethylcamphor at High Temperatures and under High Pressures. By catalytically reducing dimethylcamphor at 220–230°C. in hydrogen of 60 atmospheres pressure in the presence of reduced nickel, the following results were obtained.

No.	Sample	(g.)	Initial press. (atm.)	React. temp. °C	React. time (hrs)	H_2 absorbed (mol)
1	dimethylcamphor	30	57	220—230	27½	1.1
2	dimethylcamphor abs. alcohol	30 40	60	200	20	1.1
3	dimethylcamphor acetic acid	30 0.3	60	220—230	25	1.1
4	dimethylcampbor	30	49	280	10	2.1

(37) H. Meyer, Org. Chem. Method., Bd., I, 1126, 4. Aufl.

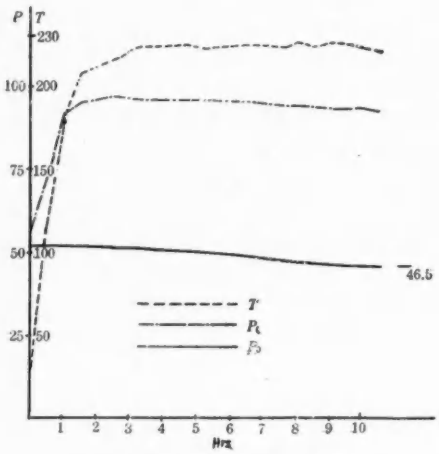


Fig. 19. (1). Dimethylcamphor.

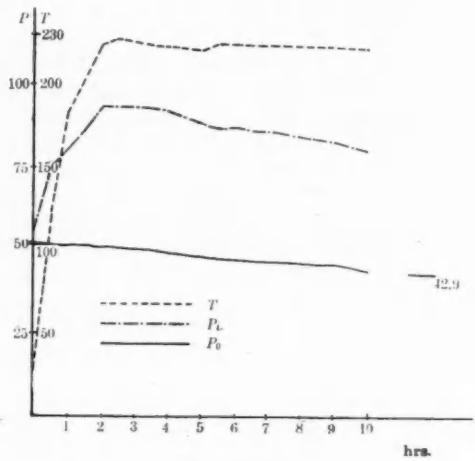


Fig. 19. (2).

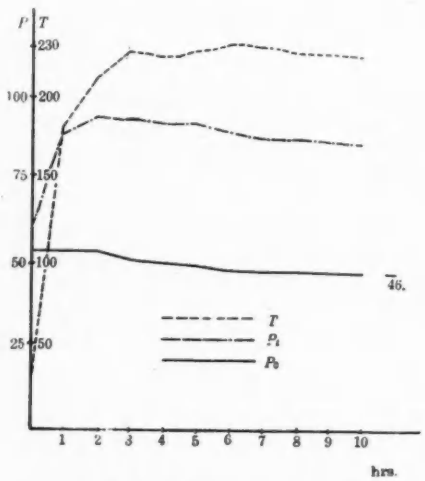


Fig. 20. (1). Dimethylcamphor + Acetic acid.

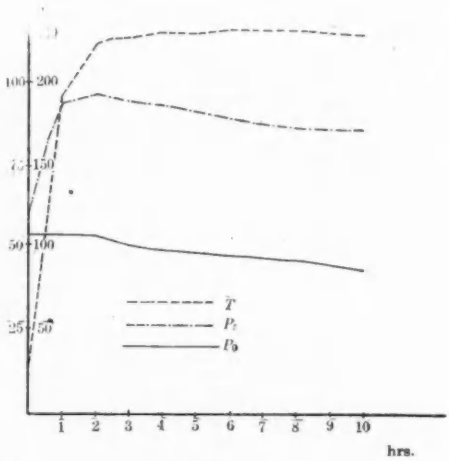


Fig. 20. (2)

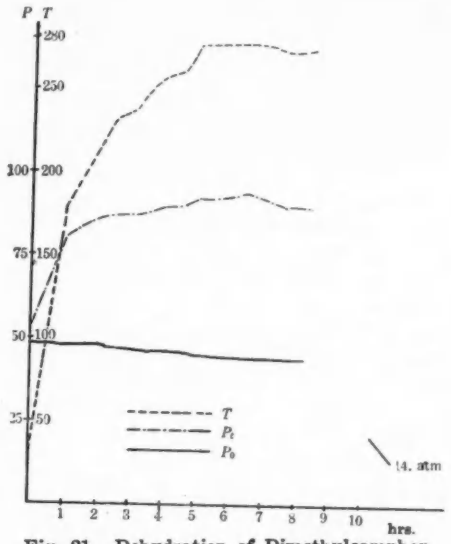


Fig. 21. Dehydration of Dimethylcamphor.

No.	Reaction product						
	Yield (g.)	d_4^{25}	n_D^{25}	$[\alpha]_D$ in alcohol	Dimethyl-camphor (%)	Dimethyl-borneol (%)	Dimethyl-isoborneol (%)
1	26	0.927	1.474	+48	80	85	15
2	24	0.948	1.475	+77	63	66	34
3	26	0.949	1.479	+59	51	86	14
4	26	0.876	1.470	−26			

In the case of sample (4), some water being mixed in the reaction product, dehydration had occurred undoubtedly. After distilling several times at ordinary pressure, the following two fractions were separated.

Fraction	B.p. °C	Yield (g.)	d_4^{25}	n_D^{25}	$[\alpha]_D$ (in alcohol)	M. R.	
						obs.	calc. for $C_{12}H_{22}$
(1)	197–200	1.9	—	—	—	—	—
(2)	200–203	20.6	0.8706	1.4695	−28.07	53.17	53.22

The elementary analysis of fraction (2) is; Found: C, 86.39; H, 13.51. Calculated for $C_{12}H_{22}$: C, 86.75; H, 13.25%.

(To be continued.)

On the Catalytic Action of Japanese Acid Earth. XI. The Isomerisation of Aldehydes to Ketones and the Explanation of the Migration of the Radicals from the Standpoint of the Electronic Theory (*Continued*).

By **Koshiro ISHIMURA.**

(Received May 14, 1941.)

Experimental. *Benzoyl carbinol.* Various methods of obtaining benzoyl carbinol have been tried by the author. Acetophenone was brominated by R. Möhlaus'[38] method in glacial acetic acid. Interaction of the resulting ω-bromacetophenone with potassium acetate was carried out more smoothly by R. Stroemer's[39] method than by W. L. Evans'[40] method, while the hydrolysis of the acetate according to the latter's information gave a better result. But I. Fischer and M. Busch's[41] method of hydrolysing it by boiling with the excess of barium carbonate in hot water about fifty times as much as the amount of the acetate gave the best. Benzoyl carbinol thus obtained has one molecule of water of crystallisation when recrytallised from hot water, m.p. 73–74°C. On standing it in a desiccator under the reduced pressure for about five hours the water of crystallisation was set free, giving anhydrous crystal, m.p. 86–87°C. Evans gave the m.p. 85–86°C., while J. Plöchl and F. Blümlein[42] 86–87°C.

α-Phenyl α-p-tolyl ethylene glycol. Anhydrous benzoyl carbinol (27 g.) dissolved in ether was added into the Grignard reagent prepared from *p*-tolyl iodide (110 g.) and magnesium ribbon (10 g.). As the solubility of the carbinol in ether is not so great, it was put in Soxlet's apparatus connected with the flask containing the reagent. The content of the flask was gently boiled so that the carbinol was gradually extracted by hot ether and the solution flowed down into the flask. When all the carbinol was dissolved the reaction mixture was left to stand overnight. It was treatd with a mixture of ice water (500 g.) and glacial acetic acid (25 c.c.). The ethereal layer was separated from the water layer which was extracted with ether several times. The combined ethereal solution was washed with dilute solution of sodium hydroxide, with water and then with a saturated solution of sodium bisulphite in order to remove the remaining carbinol. It was again washed with dilute solution of sodium hydroxide and water, concentrated by distillation till about 100 c.c. of the solution remained. On cooling a large amount of *pp'*-ditolyl produced by the side reaction crystallised out. The solution freed from the solid matter was distilled in steam and a considerable quantity of *pp'*-ditolyl, iodotoluene and toluene came over thereby. Without the previous

(38) *Ber.*, **15** (1882), 2465.
(39) *Ber.*, **39** (1906), 2294.
(40) *Am. Chem. J.*, **35** (1906), 120.
(41) *Ber.*, **24** (1894), 2680.
(42) *Ber.*, **16** (1883), 1292.

removal of these impurities, the purification of the required glycol often became very difficult. The contents of the distilling flask were extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and the solvent was removed. The required glycol was solidified on cooling. Yield about 26 g. It was recrystallised from petroleum benzine in colourless fine needles, m.p. 84.5–85.5°C. (Found: C, 78.9; H, 7.3. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.0%).

The benzoyl derivative was obtained by dissolving the glycol (0.8 g.) in ether (10 c.c.) and adding benzoyl chloride (3 g.) and sodium hydroxide (3 g.) dissolved in water (20 c.c.) and by shaking the mixture vigorously. The reaction heat evolved thereby was removed away by cooling with water intermittently. The ethereal layer was washed with water, dried over anhydrous sodium sulphate and the ether removed, leaving colourless sylup which on the addition of a small quantity of alcohol solidified immediately. It did not tend to crystallise for several days, if not treated as stated above. It formed colourless plates from dilute alcohol, m.p. 136°C. (corr.). (Found: C, 79.0; H, 6.2. $C_{22}H_{20}O_3$, monobenzoyl derivative requires C, 79.5; H, 6.0; $C_{29}H_{24}O_4$, dibenzoyl derivative, C, 79.8; H, 5.5%). Mol. wt., found (Rast), 344. $C_{22}H_{20}O_3$ requires 332 whereas $C_{29}H_{24}O_4$ 436. The substance was therefore the monobenzoyl derivative.

*Oxidation of α-phenyl α-*p*-tolyl ethylene glycol to phenyl* p*-tolyl ketone.* The glycol (0.5 g.) was added by portions into the solution of chromic oxide (0.55 g.) dissolved in 80% acetic acid (30 c.c.), and the mixture was left to stand overnight. It was heated for 30 minutes on the water bath, cooled and poured into water (400 c.c.) and then cooled with ice and salt. White crystals (0.37 g.) were thrown down which when washed with water and recrystallised from dilute alcohol melted at 57–57.5°C. (uncorr.) alone or mixed with the specimen of phenyl *p*-tolyl ketone which was obtained from toluene and benzoyl chloride and melted at the same temperature. (Found: C, 85.9; H, 6.7. $C_{14}H_{12}O$ requires C, 85.7; H, 6.1%). According to Th. Zinke[43] the stable modification of the ketone melted at 59–60°C. and the metastable at 55°C, while K. Schaum, K. Schäling and F. Klausing[44] gave the m.p. 55 and 52°C. respectively.

Phenyl p*-tolyl acetaldehyde.* The mixture of *α*-phenyl *α-p*-tolyl ethylene glycol (16 g.), water (40 c.c.) and 9 drops of concentrated sulphuric acid was heated in a sealed tube at 180–185°C. for 3 hours. When cooled down the contents were extracted with ether, washed with dilute solution of sodium carbonate, shaken with saturated solution of sodium bisulphite, the addition compound of which with the required aldehyde, white crystalline powder, was collected. Yield, 19 g. The addition compound (15 g.) was decomposed by 15% sodium hydroxide solution (50 c.c.), the aldehyde set free was extracted with ether and distilled under reduced pressure after separated from the solvent. The pure aldehyde (6.7 g.) thus obtained boiled at 176°C. (corr.) under 7 mm. It formed a colourless and almost odourless oil, tinged fuchsin sulphurous acid with pink colour when pure, while the specimen mixed with a trace of impurity prussian blue. d_4^{25}, 1.0785; n_D^{25}, 1.5844; M. R., 65.20; calculated (Eisen-

(43) Cited by C. Bodewig, *Ann. d. Physik*, **158** (1876), 234.
(44) *Ann.*, **411** (1911), 188.

lohr), 64.28. (Found: C, 85.9; H, 6,7. $C_{15}H_{14}O$ requires C, 85.7; H, 6.6%). On long standing its analytical data showed gradual decreases in the contents of both carbon and hydrogen suggesting the autoxidation of the aldehyde with atmospheric oxygen. The oxime of the aldehyde formed oil at the ordinary temperature. The semicarbazone was obtained by standing overnight a mixture of the aldehyde (2 g.), potassium acetate (2 g.), semicarbazide hydrochloride (2 g.), dissolved in hot 95% alcohol (20 c.c.) diluted with water (10 c.c.). It crystallised from dilute alcohol in colourless columns (3.0 g.) m.p. 158–159°C. (corr.) (Found: N, 16.0. $C_{16}H_{17}ON_3$ requires N, 15.7%). M. Tiffeneau and J. Lévy[45] obtained the same aldehyde by the isomerisation of α-phenyl β-tolyl ethylene oxide and gave the following data: b.p., 180–185°C./10 mm.; n_D^{16}, 1.582; m.p. of the semi-carbazone, 157–158°C.

Oxidation of phenyl p-*tolyl acetaldehyde.* Silver nitrate (1.2 g. in 1 c.c. water) was added to the alcoholic solution of the aldehyde (0.8 g. in 15 c.c.) and then potassium hydroxide (0.9 g. in 10 c.c. water) was added gradually, the mixture was shaken for 3 hours and left to stand overnight. It was filtered, the filtrate was concentrated on the water bath, and acidified with dilute sulphuric acid. An oily substance separated out which solidified on cooling. Yield. 0.5 g. Phenyl *p*-tolyl acetic acid thus obtained was recrystallised from dilute alcohol with the addition of active charcoal forming colourless plates, m.p. 115° (Found: C, 79.1; H, 6.6. $C_{15}H_{14}O_2$ requires C, 79.6, H, 6.2%). M. Tiffeneau and J. Lévy[45] gave the m.p. 112–115°C.

Isomerisation of phenyl p-*tolyl acetaldehyde.* The isomerisation was carried out as stated above (p. 199*). The aldehyde (12.0 g.) was passed over Japanese acid earth (25 g) drop by drop with a rate of 3.5 g. per hour. The reaction products consisted of (i) colourless easily-flowing liquid (2.0 g.) with a faint fluorescence mixed with water drops, (ii) colourless fragrant viscous oil (5.0 g.) which flowed out of the tube when the temperature of the furnace was raised to 350°C. after the total aldehyde was passed into it, and solidified to colourless crystalline mass, and (iii) a reddish brown viscous liquid (2.0 g.) mixed with a small quantity of crystals, obtained when the temperature was raised to 450°C.

The product (i) was separated from water drops and distilled over metallic sodium giving colourless liquid (1.0 g.), b.p. 80–112°C, d_4^{24} 0.8690, n_D^{18} 1.4997. It proved to be a mixture of about 20% benzene and about 80% toluene, when calculated from the specific gravity or from the refractive index. The product (ii) consisted of almost pure phenyl *p*-methylbenzyl ketone. (Found: C, 85.9; H, 6.7. $C_{15}H_{14}O$ requires C, 85.7; H, 6.6%). After recrystallised from dilute alcohol several times it melted at 97°C. alone or mixed with the authentic specimen synthesised from ω-bromacetophenone and toluene by Friedel-Crafts' reaction. A. Mckenzie, A. K. Mill and J. R. Myles[46] gave the m.p. 95–96°C., while M. Tiffeneau[47]

(45) *Bull. soc. chim.*, **49** (1931), 1744.

* All the samples of the acid earth used throughout this series of experiments were taken from one and the same stock, and the electric furnace as well as the reaction tube were also the same ones. This Bulletin, **16** (1941), 199.

(46) *Ber.*, **63** (1930), 908.

(47) *Compt. rend.*, **139** (1904), 1507.

94–95°C. The oxime of the ketone obtained by K. Auers'[48] method formed colourless needles melting sharply at 101°C. after recrystallisation several times from either dilute alcohol or from ligroin. H. Strassmann[49] gave the m.p. 109°C. and A. Mckenzie, A. K. Mill and J. R. Myles[50] 108–109°C. (Found: N, 6.7. $C_{15}H_{15}ON$ requires N, 6.2%).

p-Tolyl benzyl ketone, isomeric to the above one, was not found to be present in the reaction product of the present experiment. The specimen synthesised from acetyl chloride and toluene melted at 110–110.5°C. H. Strassmann[51] gave the m.p. 109°C., while M. Tiffeneau[52] 108–109°C. Its semicarbazone was obtained by heating a mixture of the ketone (0.2 g.), semicarbazide hydrochloride (0.2 g.) and potassium acetate (0.2 g.), dissolved in dilute alcohol (3 c.c.). After three day's standing long glittering needles (0.3 g.) crystallised out, which melted at 166.5°C. (corr.) after recrystallised from dilute alcohol. (Found: N, 15.4. $C_{16}H_{17}ON_3$ requires N, 15.7%). Kipping[53] obtained only azine melting at 170–173°C. by prolonged heating of the ketone with semicarbazide hydrochloride and sodium acetate and E. E. Turner[54] obtained the same product melting at 181°C. by heating the ketone with semicarbazide hydrochloride dissolved in dilute alcohol, in a sealed tube heated at 180°C. for three hours. Both the English authors reported that they could not obtain the semicarbazone. The oxime melts at 131°C. H. Strassmann[49] gave the same melting point.

Phenyl *p*-methylbenzyl ketone dissolves in concentrated sulphuric acid with a tint of canary yellow while *p*-tolyl benzyl ketone thereby develops at first dirty green which gradually changes into greenish yellow colour.

α,β-Dibenzoyl ethane. When phenyl *p*-methylbenzyl ketone was synthesised from *ω*-bromacetophenone and toluene by the Friedel and Crafts' reaction, a small quantity of colourless microcrystalline columns, m.p. 145–146°C. (uncorr.), was also obtained. It was confirmed to be *α, β*-dibenzoyl ethane produced undoubtedly by the condensation of two molecules of *ω*-bromacetophenone. (Found: C, 81.0; H, 5.8; Mol. wt., (Rast), 289. $C_{16}H_{14}O_2$ requires C, 80.7; H, 5.9%; Mol. wt., 238). S. Kape and C. Paal[55] gave it a melting point 144–145°C. and G. Dupont[56] 144°C.

p-*Methylbenzoyl carbinol.* p-Methylbenzoyl methyl acetate (30 g.) was hydrolysed by boiling with barium carbonate (30 g.) in hot water (1500 c.c.) for two hours. The solution was filtered hot. On cooling *p*-methylbenzoyl carbinol (15 g.) crystallised out, which was recrystallised from ligroin in colourless prisms, m.p. 89–90°C. (Found: C, 75.9; H, 5.4. $C_{16}H_{14}O_2$ requires C, 75.6; H, 5.5%). K. Auers[57] described it as light yellow prisms melting at 89–89.5°C., and J. Boëseken, L. W. Hansen and S. H. Bertram[58] gave a melting point 90°C. It dissolved in concentrated

(48) *Ber.*, **22** (1889), 604.
(49) *Ber.*, **22** (1889), 1231.
(50) *Loc. cit.*
(51) *Loc. cit.*
(52) *Compt. rend.*, **134** (1902), 1507.
(53) Proceeding of the Chemical Society, No. 220.
(54) *J. Chem. Soc.*, **107** (1915), 1462.
(55) *Ber.*, **21** (1888), 3056.
(56) *Compt. rend.*, **158** (1914), 1350; *Bull. soc. chim.*, (4) **15** (1914), 606.
(57) *Ber.*, **39** (1906), 3761.
(58) *Rec. trav. chim. Pays-Bas*, **35** (1916), 311.

sulphuric acid with canary yellow colour which faded away on dilution with water.

α-m-*Tolyl α*-p-*tolyl ethylene glycol.* *p*-Methylbenzoyl carbinol (28 g.) dissolved in ether was gradually added to the Grignard reagent prepared from *m*-iodotoluene (140 g.) and magnesium ribbon (14 g.) and the solution was boiled for 5 hours. As the solubility of the carbinol in ether is relatively small, a Soxlet's flask was very useful to carry out the reaction as in the case of the preparation of *α*-phenyl *α*-*p*-tolyl ethylene glycol. The contents of the reaction flask formed two layers which became one on concentration on the water bath. It was treated with a solution of glacial acetic acid (28 g.) in ice water (800 c.c.). Two layers again appeared, the upper layer was combined with the ethereal extract of the lower one, washed with dilute sodium carbonate solution and with water, shaken mechanically with saturated solution of sodium bisulphite for 10 hours to remove the remaining *p*-methylbenzoyl carbinol. It was washed with dilute aqueous sodium hydroxide and with water, the ether was removed by distillation and the residue was subjected to steam distillation for about 35 hours until no more oily substance came over. The contents of the distilling flask turned turbid white with amber coloured oil at the bottom. On cooling to −15°C. white powder was thrown down from the solution and the amber coloured oil became viscous mass (39 g.). Both were recrystallised from a large amount of hot water and then from petroleum ether giving colourless powder of *α*-*m*-tolyl *α*-*p*-tolyl ethylene glycol, m.p. 59–60°C. (Found: C, 79.0, 79.6; H, 7.2, 7.5. $C_{16}H_{18}O_2$ requires C, 79.3, H, 7.4%). Monobenzoyl derivative was obtained by Schotten-Baumann's method. It crystallised from 95% alcohol in colourless columns with one molecule of water of crystallisation, m.p. 173–174°C. (corr.) (decomp.). (Found: C, 75.6, 75.9; H, 6.7, 6.2%; Mol. wt. (Rast), 370. $C_{23}H_{22}O_3 \cdot H_2O$ requires C, 75.8; H, 6.6%; Mol. wt., 364). The water of crystallisation was not set free by heating at 57°C. under the reduced pressure of 7 mm. for 1 hour or at 120°C. under 760 mm. for 2 hours.

Oxidation of *α*-m-*tolyl α*-p-*tolyl ethylene glycol.* The glycol (0.14 g.) was dissolved in 80% acetic acid (10 c.c.) and chromic oxide (0.15 g) was added by portons into the solution, the solution was heated on the water bath for 20 minutes, diluted with water and cooled to −5°C. when white granules of *m*-tolyl *p*-tolyl ketone were obtained. It crystallised from dilute alcohol in long blades or prisms, m.p. 72°C. Yield 0.1 g.

m-*Tolyl* p-*tolyl acetaldehyde.* *α*-*m*-Tolyl *α*-*p*-tolyl ethylene glycol (50 g.) was boiled gently with a mixture of crystalline oxalic acid (125 g.) and water (50 c.c.) in an oil bath for 3 hours. The temperature of the boiling mixture was maintained at 115–120°C. while that of the bath showed 150–160°C. After cooling, it was extracted with ether, the ethereal extract was washed with dilute aqueous solution of potassium hydroxide and with water, dried over anhydrous sodium sulphate. The ether was removed and the residue was distilled in vacuo. 29.1 g. of the raw aldehyde came over boiling between 160°C. and 180°C. under 5 mm. It was purified through the addition compound with sodium bisulphite. *m*-Tolyl *p*-tolyl acetalydehyde thus obtained boiled at 182°C. (corr.) under 7 mm., d_4^{20}, 1.0684; n_D^{20}, 1.5803; M.R., 69.81; calculated (Eisenlohr), 68.90. (Found: C, 85.2; H, 7.6. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%). The semicarbazone

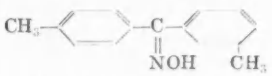
was produced by adding the aldehyde (1 g.) to a mixture of potassium acetate (1 g.) and semicarbazide hydrochloride (1 g.) dissolved in dilute alcohol (10 c.c. of 95% alcohol and 6 c.c. of water) and heating to make a clear solution. On cooling white crystals (1.1 g.) were formed. It was recrystallised from dilute alcohol in long prisms, m.p. 179–180°C. (corr.) (decomp.) (Found: N, 15.0. $C_{17}H_{19}ON_3$ requires N, 14.9%).

m-*Tolyl* p-*tolyl acetic acid.* Silver nitrate (10 g. in 10 c.c. water) was added to *m*-tolyl *p*-tolyl acetaldehyde (5 g.) dissolved in 95% alcohol (100 c.c.), followed by potassium hydroxide (7.5 g. in 70 c.c. water). 5 c.c. of the potash solution were added at a time every 10 minutes and the vessel was well shaken after each addition. After all the potash was added shaking was continued for further 3 hours, the reaction mixture was filtered and the filtrate was saturated with carbon dioxide and concentrated on the water bath. An oily substance separated out and floated on the surface, which solidified on cooling and confirmed to be *m*-tolyl *p*-tolyl ketone. The solution removed from the above ketone was neutralised with dilute sulphuric acid. Impure *m*-tolyl *p*-tolyl acetic acid separated thereby as an oily substance which on cooling turned to semi-solid mass. It was dissolved in alkali leaving a small quantity of *m*-tolyl *p*-tolyl ketone as an insoluble oil, and the solution again neutralised by the mineral acid. These steps of purification were repeated several times and finally *m*-tolyl *p*-tolyl acetic acid (0.2 g.) was recrystallised from hot water in pure state. It formed long prisms, m.p. 93–94°C. (Found: C, 79.5; H, 7.3%. Equiv. wt. (by titrating with 1/20 N NaOH), 240.1. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%; Equiv. wt., 240.1).

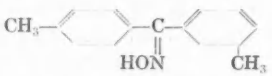
m-*Tolyl* p-*tolyl ketone.* As stated above, a considerable quantity of this ketone was produced when *m*-tolyl *p*-tolyl acetaldehyde was oxidized by moist silver oxide. It was also found to be present as less reactive substance with sodium bisulphite than *m*-tolyl *p*-tolyl acetaldehyde when the latter was purified through the addition product, and likewise obtained by the oxidation of *α*-*m*-tolyl *α*-*p*-tolyl ethylene glycol by chromic acid in acetic acid as mentioned above. The Friedel Crafts' reaction between *m*-toluyl chloride and toluene also gave the same ketone. All these specimens melted at 72°C. alone or mixed with one another, and gave the analytical data conforming with the formula. (Found: C, 85.2; H, 7.2%. Mol. wt. (Rast), 226, (cryoscopic in benzene), 218. $C_{15}H_{14}O$ requires C, 85.7; H, 6.6%. Mol. wt., 210). J. Lavaux[59] obtained the ketone by the oxidation of *m*,*p*-ditolylmethane finding the melting point 70.5°C, while W. Scharivin and Schorygin[60] gave 82°C., probably a typographical error for 72°C. The semicarbazone was obtained by standing the hot solution of the ketone (0.2 g.), semicarbazide hydrochloride (0.2 g.) and potassium acetate (0.2 g.) dissolved in dilute alcohol (2 c.c.) for 22 days. The solution of the mixture had been heated and shaken every morning and on the 22nd day the content of the flask was first found solidifing to a semi-solid mass. It crystallised from dilute alcohol in flat prisms, m.p. 177–179°C. (corr.). Lavaux[59] gave the melting point 180°C. The oxime of the ketone was obtained by adding aqueous sodium hydroxide (0.7 g. in 2 c.c.

(59) *Chem. Zentr.*, **1910 II**, 1386.
(60) *Ber.*, **36** (1903), 2027.

water) into the alcoholic solution of the ketone (0.4 g. in 7 c.c. alcohol) mixed with hydroxylamine hydrochloride (0.4 g. in 2 c.c. water) and by the subsequent heating of the mixture for a while. The reaction mixture was left to stand overnight and neutralised with dilute hydrochloric acid. An oil separated which soon solidified. It melted at 119–129° when recrystallised once from dilute alcohol. By the fractional crystallisation over twenty times from dilute alcohol two fractions melting at 119–121°C. (A) and 133–134°C. (B) were obtained. J. Lavaux[59] obtained the oxime melting at 128–129°C. and W. Scharivin and Schorygin[60] two isomers melting at 118–119°C. and 143°C. respectively. Both (A) and (B) were sujbected to the Beckmann rearrangement by the action of phosphorus pentachloride in ether solution giving two isomeric toluyl toluidides melting at 104°C. (glittering scales from dilute alcohol) and 111–112°C. (silky needles from the same solvent) respectively. (Found: N, 6.8 for the former, 6.1 for the latter. $C_{15}H_{15}ON$ requires N, 6.2%). The former (m.p. 104°C.) was confirmed to be *p*-toluyl *m*-toluidide by the mixed melting point with the specimen synthesised form *p*-toluic acid and *m*-toluidine, while the latter (m.p. 111–112°C.) *m*-toluyl *p*-toluidide, the same product as that from *m*-toluic acid and *p*-toluidine. The configurations of the oximes, therefore, are as follows:—



(A) (m.p. 119-121°C.)



(B) (m.p. 133-134°C.)

p-*Tolyl* m-*methylbenzyl ketone*. As one of the starting materials for the preparation of the above ketone *m*-xylene was taken. It was first brominated and then interacted with potassium cyanide following the informations given by E. F. J. Atkinson and J. F. Thorpe[61] and A. F. Titley[62] respectively. *m*-Xylyl cyanide thus obtained was converted to *m*-tolyl acetamide by Br. Radziszewski and P. Wispek's method,[63] which (5 g.) on boiling with concentrated hydrochloric acid (15 c.c.) gave m-tolyl acetic acid (3.5 g.). The acid (5 g.) was boiled with thionyl chloride (20 c.c.) on the water bath for 2 hours, the excess thionyl chloride was driven by evacuation and the residue distilled in vacuo giving pure *m*-tolyl acetyl chloride (5 g.). At every step of the above preparation the fractional distillation or fractional crystallization was carried out in order to remove the isomeric impurities as far as possible. The most effective separation from isomers was now found to be performed by the fractional crystallization of the acid amides from hot water. P. Hill and W. F. Short[64] reported the inseparability of the mixture of ortho and para isomers of xylyl bromides, chlorides, cyanides, acetates or alcohols and tolyl acetic acids by fractionations as already stated.

m-Tolyl acetyl chloride (5 g.) thus obtained was added drop by drop to toluene (30 c.c.) mixed with anhydrous aluminium chloride (5 g.). After 4 hour's standing all the aluminium chloride was dissolved. The

(61) *J. Chem. Soc.*, **91** (1907), 1699.
(62) *J. Chem. Soc.*, **1926**, 514.
(63) *Ber.*, **18** (1885), 1282.
(64) *J. Chem. Soc.*, **1935**, 1126.

reaction mixture was poured into ice water (150 c.c.), the upper layer was separated, combined with the toluene extract of the lower layer, washed with dilute caustic potash and with water, dried over anhydrous sodium sulphate. On distilling off the toluene a blackish brown mass (8 g.) was obtained, which was recrystallised from dilute alcohol several times with the addition of active charcoal and gave the required ketone which formed colourless long flat needles (3.1 g.), m.p. 68°C. (Found: C, 85.8; H, 7.4. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%). The ketone dissolves in concentrated sulphuric acid tinging it with a canary-yellow colour. The semicarbazone crystallised in colourless needles from dilute alcohol, m.p. 192–194°C. (uncorr.) (with slight decomp.). (Found: N, 14.8. $C_{17}H_{19}ON_3$ requires N, 14.9%).

The oxime formed also colourless needles when recrystallised from dilute alcohol, m.p. 108–109°C. (Found: N, 6.3. $C_{16}H_{17}ON$ requires 5.9%).

m-*Tolyl* p-*methylbenzyl ketone*. The ketone was synthesised in two ways.

(a) *p*-Tolyl acetonitrile (6 g.) dissolved in ether (50 c.c.) was added to the Grignard reagent prepared from *m*-iodotoluene (40 g.) and magnesium ribbon (4.4 g.), the reaction mixture was boiled for 10 hours, treated with cold dilute sulphuric acid (20 g. conc. acid in 800 c.c. ice water). The required ketone was produced as ketimine sulphate dissolved in the water layer, which was separated, washed with ether and heated gently on the water bath. The ketone was liberated as a reddish oil floating on the surface. It was extracted with ether, washed with water, dried over anhydrous sodium sulphate and the ether was driven off. A brownish oil (1.4 g.) thus obtained solidified on cooling to −15°C., which crystallised from dilute alcohol in colourless fine needless, m.p. 40–41°C. (Found: C, 85.4; H, 7.4. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%).

(b) The ketone was obtained by the oxidation of the corresponding alcohol, which was in its turn obtained by the interaction of p-tolyl acetaldehyde with *m*-tolyl magnesium iodide. The *p*-tolyl acetaldehyde was prepared by dehydration of *p*-tolyl ethylene glycol produced by the catalytic hydrogenation of *p*-methylbenzoyl carbinol in the following way.

A colloidal solution of platinum was obtained by passing hydrogen into the solution of chloroplatinic acid (1.5 g., calc. as Pt) and gum arabic (1 g.) in dilute acetic acid (50 c.c. acid in 120 c.c. water) with platinum black (0.03 g.) suspended in the solution. *p*-Methylbenzoyl carbinol (13.1 g. dissolved in 80 c.c. glacial acetic acid) was added to the above colloidal solution and the mixture was shaken in the atmosphere of hydrogen at the ordinary temperature and pressure. 1800 c.c. (22°C, 761 mm.) of hydrogen were absorbed in 60 minutes. Caustic soda (85 g. dissolved in a small quantity of water) was added to the solution. Care must be taken not to make the solution alkaline, as otherwise the next step i.e. the extraction with ether would become difficult. It was extracted with a large amount of ether, the ethereal extract washed with dilute alkali and with water, dried over anhydrous sodium sulphate and the ether was removed by distillation. The residue (11 g.) solidified on standing. The raw p-tolyl ethylene glycol thus obtained crystallised from petroleum benzine in glittering scales, m.p. 76.5–77.5°C. (Found: C, 70.5; H, 8.0. $C_9H_{12}O_2$ requires C, 71.1; H, 7.9%). The remaining *p*-methylbenzoyl car-

binol could thereby be easily removed, as it is more soluble in the solvent than the glycol though its melting point is higher than that of the glycol by about 15°. E. Späth[65] obtained diethyl ether of the glycol. No description of the free glycol was however given by him.

The raw product of *p*-tolyl ethylene glycol (8 g.) was sealed in a glass tube mixed with water (20 c.c.) and 4 drops of concentrated hydrochloric acid, heated at 180–185°C. for 4 hours. The contents of the tube were then extracted with ether, washed with water, dried over anhydrous sodium sulphate and distilled in vacuo. *p*-Tolyl acetaldehyde (2 g.) thus obtained passed over at 92–93°C. under the reduced pressure of 8 mm. which on further purification boiled at 97°C. under 10 mm.. d_4^{20}, 1.0052; n_D^{20}, 1.5255; M. R. found: 40.86; calc. (Eisenlohr) 40.17. K. Kling[66] gave the boiling point 109°C./17 mm. while E. Späth[67] 96°C./10 mm.

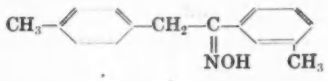
p-Tolyl acetaldehyde (2 g. dissolved in 2 c.c. ether), synthesised as stated above, was added to the Grignard reagent prepared from *m*-iodotoluene (3.5 g.) and magnesium ribbon (0.36 g.). The reaction mixture was boiled for 2 hours and left to stand overnight. It was decomposed by dilute hydrochloric acid (1.2 c.c. conc. acid in 50 c.c. ice water) and extracted withe ether, the ethereal extract was washed with dilute solution of potassium carbonate, dried over anhydrous sodium sulphate and the ether was removed by distillation. The residue was distilled in steam leaving in the flask a thick oil (0.85 g.), the raw *p*-methylbenzyl m-tolyl carbinol, which without further purification was oxidized to the corresponding ketone; the oil was dissolved in 80% acetic acid (60 c.c.) and chromic oxide (0.28 g. in 1 c.c. water) was added to it. The mixture turned at once blackish, and then green when heated on the water bath for 30 minutes. It was poured into ice water (600 c.c.). A resinous matter thus produced sticked to the bottom of the vessel, which was extracted with ether, the ethereal extract was washed with dilute caustic potash and with saturated solution of sodium chloride, dried over calcium chloride, and the ether was removed leaving viscous matter (0.53 g.). It solidified on long standing at −15°C. It was recrystallised from dilute alcohol giving a small quantity of the required ketone melting at 40–41°C.

The semicarbazone was not obtained even after 140 days' standing of the solution of the ketone (0.2 g.), semicarbazide hydrochloride (0.2 g.) and potassium acetate (0.2 g.) in dilute alcohol, only a small quantity of white powder being thereby produced which decomposed at about 250°C.

The oxime was obtained in the usual way; the ketone (0.08 g.) and hydroxylamine hydrochloride (0.14 g.) were dissolved in hot dilute alcohol (2 c.c.), the solution was left to stand overnight and neutralized with dilute sulphuric acid. An oil (0.06 g.) was thrown down which on cooling solidified. It crystallised from dilute alcohol in colourless needles, m.p. 88.5°C. It was subjected to the Beckmann rearrangement; phosphorus pentachloride (0.05 g.) was added to the ether solution of the oxime (0.05 g. in 2 c.c. ether), which was shaken for 15 minutes and poured into ice water. White granules separated and was recrystallised from dilute

(65) *Monatsh.*, **37** (1916), 9.
(66) *Chem. Zentr.*, **1908, I**, 951.
(67) *Ber.*, **47** (1914), 767; *Monatsh.*, **37** (1916), 9.

alcohol in colourless plates or from ligroin in needles, m.p. 123–124°C., which was not depressed by the mixing of [*p*-tolyl-acetyl]-*m*-toluidide synthesised from *p*-tolyl acetic acid and *m*-toluidine, showing that the original oxime was of the following anti-*p*-methylbenzyl configuration:—



(Found: N, 5.9. $C_{16}H_{17}ON$ requires N, 5.9%). *m*-Toluyl *p*-methylbenzylamine, the compound isomeric to [*p*-tolyl-acetyl]-*m*-toluidide, was obtained by the condensation of m-toluic acid and *p*-methylbenzylamine, colourless leaflets from dilute alcohol, m.p. 116°C. (Found: N, 6.3, $C_{16}H_{17}ON$ requires N, 5.9%). *m*-Tolyl *p*-methylbenzyl ketone was oxidized slowly by atmospheric oxygen giving *p*- and *m*-toluic acids; on long standing white granules deposited on the wall of the vessel containing the ketone, which were separated into the above mentioned two isomeric acids by the fractional crystallisation from hot water, melting at 179°C. and 110°C. respectively alone or mixed with the authentic specimens.

Isomerization of m-tolyl p-tolyl acetaldehyde. The aldehyde (13.5 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C. at a rate of 3.8 g. per hour, being accompanied by the slow current of carbon dioxide. A heavy yellowish brown oil covered by the thin layer of toluene (7.5 g. in total) was collected in the receiver during the passing of the aldehyde and the lapse of 1 hour after it. The temperature of the tube was then raised to 350°C. under the reduced pressure of 30 mm. and a thick brownish red oil (0.7 g.) was obtained. Both the products showed no colour reaction characteristic to aldehydes. They were combined, washed with dilute aqueous potassium hydroxide, with the saturated solution of sodium chloride and dried over calcium chloride. The calcium chloride was washed with ether to remove the absorbed reaction products, the ether was evaporated up and the residue was combined with the main part, which was distilled under the reduced pressure of 5 mm. giving the following fractions:—

Table 1.

Fraction	B.p. (°C)	Yields (g.)	Remarks
(1)	140–167	1.1	Light yellow oil with aromatic odour.
(2)	167–175	1.3	Light yellow oil, almost odourless.
(3)	175–180	4.0	Almost all amount came over constantly at 177°C. Odourless, yellow viscous oil.
(4)	Above 180	0.7	Very viscous, reddish brown oil.
		Total 7.1	

The alkaline washing liquid of the reaction product before subjected to the distillation was concentrated on the water bath and neutralised by dilute sulphuric acid. Oil drops were thrown down which crystallised on

cooling (0.01 g.). They were recrystallised from hot water and found to be a mixture of *p*- and *m*-toluic acids.

The third fraction in Table I (b.p. 175–180°C./5 mm.) made the main part of the reaction products. It did not tend to solidify when cooled. 0.5 g. of it gave the solid oxime (0.4 g.), colourless needles, m.p. 86.5–87.5°C., which was confirmed to consist of *m*-tolyl *p*-methylbenzyl ketoxime exclusively. The oxime was identified by the mixed melting point with the authentic specimen as well as by the formation of [*p*-tolyl-acetyl]-*m*-toluidide by the Beckmann rearrangement. *p*-Tolyl *m*-methylbenzyl ketoxime was not found to exist in it, the fact which was also confirmed in the cases of the other fractions in Table 1. It may, therefore, safely be mentioned that in the molecule of *m*-tolyl *p*-tolyl acetaldehyde the migration of *m*-tolyl radical exclusively took place under the experimental condition given above.

In one run of the experiment carried out under the same condition, the reaction product was left to stand for just three months. A considerable quantity of white deposit was formed in the vessel containing the oily product, which revealed itself as a mixture of *m*- and *p*-toluic acids melting at 110 and 179°C. respectively when separated by the fractional crystallisation from hot water. The acids were most probably formed by the oxidation of *m*-tolyl *p*-methylbenzyl ketone with atmospheric oxygen.

(To be continued.)

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Studien über Oxydationszersetzung des Methans.

Von Toyoziro OGURA.

(Eingegangen am 6. Juni, 1941.)

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VIII. Zusammenfassung. Schlusswort.

I. Einleitung und Literatur. Die Oxydation des Methans kann man, von dem Gesichtspunkte der Reaktionsprodukte aus, in folgende drei Klassen einteilen. Die Erste ist die sogenannte Verbrennung, wobei Wasser, Kohlendioxyd oder Kohlenoxyd durch die Einwirkung des Sauerstoffs entstehen. Die Zweite ist die Oxydationszersetzung, in welcher sich Wasserstoff, Kohlendioxyd oder Kohlenoxyd bilden. Die Dritte ist die unvollkommene Oxydation; es werden dabei sauerstoffhaltige Verbindungen niederer Klasse, z.B. Methanol, Formaldehyd, Ameisensäure, Essigsäure, Azeton u.s.w. gebildet.

Tafel 1 veranschaulicht die oben erwähnten Verhälnisse.

Tafel 1.

A. Verbrennung.

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O + 191.8\ \text{Kcal.}$$
$$2\,CH_4 + 3\,O_2 = 2\,CO + 4\,H_2O + 247.8\ \text{Kcal.}$$
$$CH_4 + 3\,CO_2 = 4\,CO + 2\,H_2O - 79.8\ \text{Kcal.}$$

B. Oxydationszersetzung.

$$2\,CH_4 + O_2 = 2\,CO + 4\,H_2 + 16.6\ \text{Kcal.}$$
$$CH_4 + O_2 = CO_2 + 2\,H_2 + 76.2\ \text{Kcal.}$$
$$CH_4 + O_2 = CO + H_2 + H_2O + 66.1\ \text{Kcal.}$$
$$CH_4 + 2\,CO_2 = 3\,CO + H_2 + H_2O - 69.7\ \text{Kcal.}$$
$$CH_4 + H_2O = CO + 3\,H_2 - 49.5\ \text{Kcal.}$$
$$CH_4 + 2\,H_2O = CO_2 + 4\,H_2 - 39.4\ \text{Kcal.}$$
$$CH_4 + CO_2 = 2\,CO + 2\,H_2 - 59.6\ \text{Kcal.}$$

C. Unvollkommene Oxydation.

$$\left.\begin{matrix} CH_4 + O_2 \\ CH_4 + H_2O \\ CH_4 + CO_2 \\ CH_4 + CO \end{matrix}\right\} \rightarrow \begin{matrix} CH_3OH,\ H\text{-}CHO,\ H\text{-}COOH, \\ CH_3\text{-}COOH \\ CH_3\text{-}CO\text{-}CH_3 \end{matrix}$$

Diese Reaktionen sind bereits einigermassen studiert: als Oxydationsmittel hat man sich einiger Gase, z.B. Sauerstoff, Wasserdampf, Kohlendioxyd und Stickstoffoxyd, bedient, ausserdem sind anorganische Oxydationsmittel, Chromsäure, Permangansäure und Bichromsäure und Metalloxyde verwendet worden.

Die Literatur darüber liegt in zielmlich grosser Menge vor, wovon ich einige Beispiele in der folgenden Tafel übersichtlich zusammengefasst habe.

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(54) Ogura, *J. Soc. Chem. Ind. Japan*, **43** (1940), 395.
(55) Pascal, Botolfsen, *Compt. rend.*, **191** (1930), 186.

Vorliegende Abhandlung ist eine Zusammenstellung meiner Arbeiten über Oxydationszersetzung des Methans, welche sich mit den notwendigen Bedingungen und den Katalysatoren befasst und die Reaktionen des Methans mit Sauerstoff, Wasserdampf und Kohlendioxyd in Klarheit gebracht haben.

Roh Methan aus Naturgas von Kinsui, Sintiku, Formosa wurde zum Experiment verwendet. Das Naturgas von Kinsui kommt aus 1000–1500 m Tiefe unter der Erde und wird nach Entfernung des Benzins durch Kerosenausspülung, in einer eisernen Leitungsröhre nach der Stadt Sintiku geleitet. Dasselbe hat folgende Komponenten.

CO_2 1.0%, C_nH_m 0.5%, Luft 1.0%, CH_4 95.0%, C_2H_6 2.5%.

Als Darstellungsmethode des Methans in Laboratorien sind folgende drei oder vier Weisen in der Literatur[1] angegeben.

1) Essigsauresnatrium, Kalk und Aetznatron.
2) Aluminiumkarbid und Wasser.
3) Zersetzung des Jodmethyl.

Diese Methoden reichen aber zur Darstellung reines Methans nicht aus. Letzteres kann man nur durch wiederholtes Distillieren unter niederer Temperatur erhalten.

Zum Experiment bediente ich mich gewöhnlicher Strömungsmethode. Die Veränderungen in der Anordnung des Apparates, die ich vorgenommen habe, sind in Abb. 1 schematisch dargestellt.

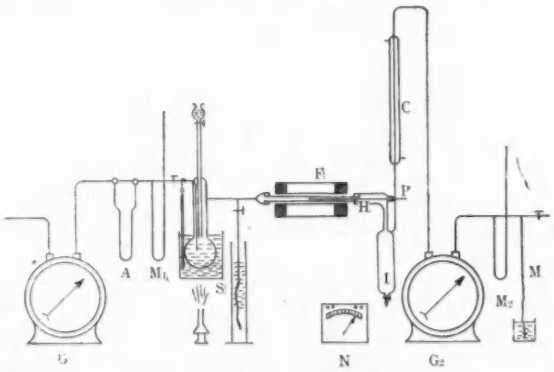

Abbildung 1. Schematische Anordnung des Apparates.

(1) L. Moser, "Reindarstellung von Gasen", 1920.
A. Klemenc, "Die Behandlung u. Reindarstellung von Gasen", 1938.
A. Farkas u. H. W. Melville, "Experimental Methods in Gas Reaktions", 1939.

Reaktionsröhre sind aus Porzellan oder Quartz, von 15–20 mm. Durchmesser und 500 mm. Länge und mit passenden Katalysatoren versehen. Ich gebrauchte Gasometer zur Messung der Gase und Kapillar-Strömungsmesser zur Bestimmung des Sauerstoffs und Kohlendioxyds. Der Wasserdampf wurde durch die Regulierung der Badetemperatur, den Kapillar-Strömungsmesser und die Menge des kondensierten Wassers kontrolliert. Dabei wurde zur Vermeidung der Kondensation des Dampfes die Leitungsröhre mittels Nichromdrahts erwärmt.

Die Gasproben, die man an beliebigen Stellen entnahm, wurde nach der Hempelschen Methode analysiert.

II. Gleichgewichtskonstanten. Die Gleichgewichtskonstanten der Reaktionen des Methans auf Wasserdampf, Sauerstoff und Kohlendioxyd sind von einigen Autoren angegeben. Diese Werte weichen aber zielmlich von einander ab.

Setzt man die Gleichgewichtskonstanten der folgenden 1–10 Reaktionen als Kp_1, Kp_2, Kp_3, Kp_4, Kp_5, Kp_6, Kp_7, Kp_8, Kp_9, Kp_{10} und die der Reaktionen 11–14 als Kp_A, Kp_B, Kp_C, Kp_D, so kann man die ersteren Werte $Kp_1 \ldots . Kp_{10}$ aus der Benutzung der letzteren Werte $Kp_A \ldots . Kp_D$, die genau festgestellt sind, berechnen. Die Werte log $Kp_A \ldots . Kp_D$ wurden nach folgenden Formeln berechnet. Tafel 2 zeigt diese Werte, Tafel 3 die Werte log $Kp_1 \ldots .$ log Kp_{10}. Abb. 2 zeigt die Kurven des log Kp und der Temperatur.

(1) $CH_4 + H_2O = CO + 3H_2$

$$Kp_1 = \frac{pCH_4 \cdot pH_2O}{p^3H_2 \cdot pCO} = \frac{pCH_4 \cdot pCO_2 \cdot pCO \cdot pH_2O}{p^2H_2 \cdot p^2CO \cdot pCO_2 \cdot pH_2} = \frac{Kp_A}{Kp_B \cdot Kp_C}$$

$$\begin{array}{rl} & CH_4 = C + 2H_2 \\ & C + CO_2 = 2CO \\ + & CO + H_2O = CO_2 + H_2 \\ \hline & CH_4 + H_2O = CO + 3H_2 \end{array}$$

$$\log Kp_1 = \log Kp_A - \log Kp_B - \log Kp_C$$

(2) $CH_4 + 2H_2O = CO_2 + 4H_2$

$$Kp_2 = \frac{pCH_4 \cdot p^2H_2O}{pCO_2 \cdot p^4H_2} = \frac{pCH_4 \cdot p^2H_2O \cdot pCO_2 \cdot p^2CO}{p^2H_2 \cdot p^2CO \cdot p^2CO_2 \cdot p^2H_2} = \frac{Kp_A}{Kp_B \cdot K^2p_C}$$

$$\begin{array}{rl} & CH_4 = C + 2H_2 \\ & C + CO_2 = 2CO \\ + & 2CO + 2H_2O = 2CO_2 + 2H_2 \\ \hline & CH_4 + 2H_2O = CO_2 + 4H_2 \end{array}$$

$$\log Kp_2 = \log Kp_A - \log Kp_B - 2 \log Kp_C$$

(3) $CH_4 + CO_2 = 2CO + 2H_2$

$$Kp_3 = \frac{pCH_4 \cdot pCO_2}{p^2CO \cdot pH_2} = \frac{Kp_A}{Kp_B}$$

$$\begin{array}{rl} & CH_4 = C + 2H_2 \\ + & C + CO_2 = 2CO \\ \hline & CH_4 + CO_2 = 2CO + 2H_2 \end{array}$$

$$\log Kp_3 = \log Kp_A - \log Kp_B$$

(4) $CH_4 + 2O_2 = CO_2 + 2H_2O$

$$Kp_4 = \frac{pCH_4 \cdot p^2O_2}{pCO_2 \cdot p^2H_2O} = \frac{pCH_4 \cdot p^2H_2O \cdot p^4H_2 \cdot p^2O_2}{pCO_2 \cdot p^4H_2 \cdot p^4H_2O} = \frac{Kp_2}{K^2 p_D}$$

$$\begin{array}{l} CH_4 + 2H_2O = CO_2 + 4H_2 \\ + \quad 4H_2 + 2O_2 = 4H_2O \\ \hline CH_4 + 2O_2 = CO_2 + 2H_2O \end{array}$$

$$\log Kp_4 = \log Kp_2 - 2 \log Kp_D$$

(5) $2CH_4 + 3O_2 = 2CO + 4H_2O$

$$Kp_5 = \frac{p^2CH_4 \cdot p^3O_2}{p^2CO \cdot p^4H_2O} = \frac{p^2CH_4 \cdot p^6H_2O \cdot p^6H_2 \cdot p^3O_2}{p^2CO \cdot p^6H_2 \cdot p^6H_2O} = \frac{K^2 p_1}{K^3 p_D}$$

$$\begin{array}{l} 2CH_4 + 2H_2O = 2CO + 6H_2 \\ + \quad 6H_2 + 3O_2 = 6H_2O \\ \hline 2CH_4 + 3O_2 = 2CO + 4H_2O \end{array}$$

$$\log Kp_5 = 2 \log Kp_1 - 3 \log Kp_D$$

(6) $CH_4 + O_2 = CO + H_2 + H_2O$

$$Kp_6 = \frac{pCH_4 \cdot pO_2}{pCO \cdot pH_2 \cdot pH_2O} = \frac{pCH_4 \cdot pH_2O \cdot p^2H_2 \cdot pO_2}{pCO \cdot p^3H_2 \cdot p^2H_2O} = \frac{Kp_1}{Kp_D}$$

$$\begin{array}{l} CH_4 + H_2O = CO + 3H_2 \\ + \quad 2H_2 + O_2 = 2H_2O \\ \hline CH_4 + O_2 = CO + H_2 + H_2O \end{array}$$

$$\log Kp_6 = \log Kp_1 - \log Kp_D$$

(7) $CH_4 + O_2 = CO_2 + 2H_2$

$$Kp_7 = \frac{pCH_4 \cdot pO_2}{pCO_2 \cdot p^2H_2} = \frac{pCH_4 \cdot p^2H_2O \cdot p^2H_2 \cdot pO_2}{pCO_2 \cdot p^4H_2 \cdot p^2H_2O} = \frac{Kp_2}{Kp_D}$$

$$\begin{array}{l} CH_4 + 2H_2O = CO_2 + 4H_2 \\ + \quad 2H_2 + O_2 = 2H_2O \\ \hline CH_4 + O_2 = CO_2 + 2H_2 \end{array}$$

$$\log Kp_7 = \log Kp_2 - \log Kp_D$$

(8) $2CH_4 + O_2 = 2CO + 4H_2$

$$Kp_8 = \frac{p^2CH_4 \cdot pO_2}{p^2CO \cdot p^4H_2} = \frac{p^2CH_4 \cdot p^2H_2O \cdot p^2H_2 \cdot pO_2}{p^2CO \cdot p^6H_2 \cdot p^2H_2O} = \frac{K^2 p_1}{Kp_D}$$

$$\begin{array}{l} 2CH_4 + 2H_2O = 2CO + 6H_2 \\ + \quad 2H_2 + O_2 = 2H_2O \\ \hline 2CH_4 + O_2 = 2CO + 4H_2 \end{array}$$

$$\log Kp_8 = 2 \log Kp_1 - \log Kp_D$$

(9) $CH_4 + 3CO_2 = 4CO + 2H_2O$

$$Kp_9 = \frac{pCH_4 \cdot p^3CO_2}{p^4CO \cdot p^2H_2O} = \frac{pCH_4 \cdot pH_2O \cdot p^3CO_2 \cdot p^3H_2}{pCO \cdot p^3H_2 \cdot p^4CO \cdot p^3H_2O} = Kp_1 \cdot K^3 p_C$$

$$\begin{array}{l} CH_4 + H_2O = CO + 3H_2 \\ + \; 3CO_2 + 3H_2 = 4CO + 3H_2O \\ \hline CH_4 + 3CO_2 = 4CO + 2H_2O \end{array}$$

$$\log Kp_9 = \log Kp_1 + 3 \log Kp_C$$

(10) $CH_4 + 2CO_2 = 3CO + H_2 + H_2O$

$$Kp_{10} = \frac{pCH_4 \cdot p^2CO_2}{p^3CO \cdot pH_2 \cdot pH_2O} = \frac{pCH_4 \cdot pH_2O \cdot p^2CO_2 \cdot p^2H_2}{pCO \cdot p^3H_2 \cdot p^2CO \cdot p^2H_2O} = Kp_1 \cdot K^2p_C$$

$$\begin{array}{l} CH_4 + H_2O = CO + 3H_2 \\ + \quad 2CO_2 + 2H_2 = 2CO + 2H_2O \\ \hline CH_4 + 2CO_2 = 3CO + H_2 + H_2O \end{array}$$

$$\log Kp_{10} = \log Kp_1 + 2 \log Kp_C$$

(11) $CH_4 = C + 2H_2 + 76.2$ Kcal. $\quad Kp_A = \frac{pCH_4}{p^2H_2}$

(12) $2CO = C + CO_2 + 135.8$ Kcal. $\quad Kp_B = \frac{p^2CO}{pCO_2}$

(13) $CO_2 + H_2 = CO + H_2O - 10.1$ Kcal. $\quad Kp_C = \frac{pCO_2 \cdot pH_2}{pCO \cdot pH_2O}$

(14) $2H_2O = 2H_2 + O_2 - 115.6$ Kcal. $\quad Kp_D = \frac{p^2H_2O}{p^2H_2 \cdot pO_2}$

Die Werte $\log Kp_A$, $\log Kp_B$, $\log Kp_C$, $\log Kp_D$, wurden nach folgenden Formeln berechnet.

$$\log Kp_A = \frac{3.798}{T} - 3.958 \log T - 1.039 \cdot 10^{-5} T + 4.76 \cdot 10^{-7} T^2 - 4.795 \cdot 10^{-11} T^3 + 7.04$$

$$\log Kp_B = \frac{-8.742}{T} + 3.731 \log Kp\, T - 2.248 \cdot 10^{-3} T + 4.76 \cdot 10^{-7} T^2 - 4.795 \cdot 10^{-11} T^3 + 0.496$$

$$\log Kp_C = \frac{-9.360}{4.571\, T} - \frac{1}{2} \log T + \frac{1}{4.571} \frac{dT}{T^2} \left[R\frac{5000}{T} + 2R\frac{9\,0}{T} + 2R\frac{3500}{T} - R\frac{3100}{T} - R\frac{2300}{T} - 2R\frac{5800}{T} \right] dT - 0.789$$

$$\log Kp_D = \frac{25119}{T} - 0.95 \log T - 0.72 \cdot 10^{-3} + 1.62 \cdot 10^{-7} T^2 - 1.601$$

Tafel 2. Die Werte $\log Kp_A$, $\log Kp_B$, $\log Kp_C$ und $\log Kp_D$.

°C	°T_K	$\log Kp_A$	$\log Kp_B$	$\log Kp_C$	$\log Kp_D$
400	673	1.481	−4.246	1.096	32.623
450	723	0.941	−3.315	0.889	29.989
500	773	0.675	−2.505	0.720	27.690
550	823	0.284	−1.795	0.571	25.667
600	873	−0.064	−1.168	0.441	23.873
650	923	−0.378	−0.611	0.326	22.269
700	973	−0.661	−0.112	0 224	20.828
750	1023	−0.919	−0.335	0.135	19.527
800	1073	−1.155	0.741	0.047	18.344
850	1123	−1.371	1.108	−0.025	17.263
900	1173	−1.569	1.444	−0.089	16.276
950	1223	−1.751	1.750	−0.149	15.366
1000	1273	−1.921	2.032	−0.205	14.527
1050	1323	−2.050	2.291	−0.254	13.749
1100	1373	−2.223	2.530	−0.297	13.029
1150	1423	−2.356	2.756	−0.342	12.358
1200	1473	−2.486	2.958	−0.381	11.733

Tafel 3. Die Werte $\log Kp_1$ ..... $\log Kp_{10}$.

°C	°T_K	$\log Kp_1$	$\log Kp_2$	$\log Kp_3$	$\log Kp_4$	$\log Kp_5$
400	673	4.637	3.547	5.727	−61.699	−88.595
450	723	3.367	2.478	4.429	−57.500	−83.233
500	773	2.460	1.740	3.180	−53.640	−78.150
550	823	1.508	0.937	2.076	−50.397	−73.985
600	873	0.663	0.222	1.104	−47.524	−70.293
650	923	−0.093	−0.419	0.233	−44.957	−66.993
700	973	−0.773	−0.997	−0.549	−42.653	−64.030
750	1023	−1.389	−1.524	−1.254	−40.578	−61.359
800	1073	−1.943	−1.990	−1.896	−38.678	−58.918
850	1123	−2.454	−2.429	−2.479	−36.955	−56.697
900	1173	−2.924	−2.835	−3.013	−35.387	−54.676
950	1223	−3.352	−3.203	−3.501	−33.597	−52.802
1000	1273	−3.748	−3.543	−3.953	−32.597	−51.077
1050	1323	−4.087	−3.833	−4.341	−31.331	−49.477
1100	1373	−4.456	−4.159	−4.753	−30.217	−47.999
1150	1423	−4.773	−4.431	−5.115	−29.147	−46.620
1200	1473	−5.063	−4.682	−5.444	−28.148	−45.325

°C	°T_K	$\log Kp_6$	$\log Kp_7$	$\log Kp_8$	$\log Kp_9$	$\log Kp_{10}$
400	673	−27.986	−29.076	−23.349	7.925	6.829
450	723	−26.622	−27.511	−23.255	6.034	5.145
500	773	−25.230	−25.950	−22.770	4.620	3.900
550	823	−24.159	−24.730	−22.651	3.221	2.650
600	873	−23.362	−23.651	−22.547	1.986	1.545
650	923	−22.362	−22.688	−22.455	0.885	0.559
700	973	−21.601	−21.825	−22.374	−0.101	−0.325
750	1023	−20.916	−21.051	−22.305	−0.984	−1.119
800	1073	−20.287	−20.334	−22.230	−1.802	−1.849
850	1123	−19.717	−19.692	−22.171	−2.529	−2.504
900	1173	−19.200	−19.111	−22.124	−3.191	−3.102
950	1223	−18.718	−18.569	−22.070	−3.799	−3.650
1000	1273	−18.275	−18.070	−22.023	−4.363	−4.158
1050	1323	−17.864	−17.582	−21.979	−4.849	−4.595
1100	1373	−17.485	−17.188	−21.941	−5.347	−5.050
1150	1423	−17.131	−16.789	−21.904	−5.799	−5.457
1200	1473	−16.796	−16.415	−21.859	−6.206	−5.825

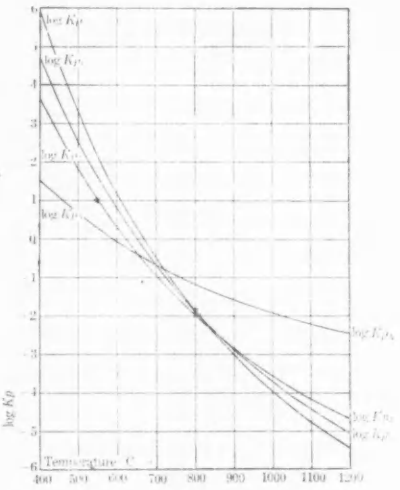

Abbildung 2.
Die Kurve $\log Kp_1$, $\log Kp_2$, $\log Kp_3$ und $\log Kp_A$.

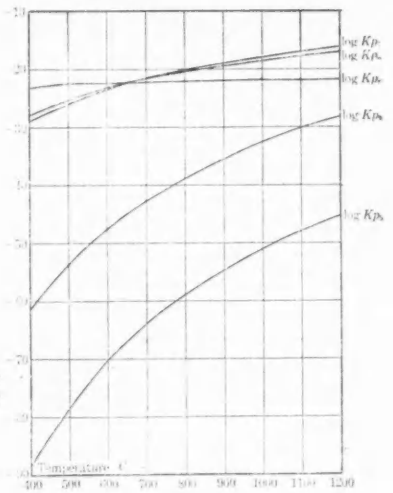

Abbildung 3.
Die Kurve $\log Kp_4$, $\log Kp_5$, $\log Kp_6$, $\log Kp_7$ und $\log Kp_8$.

Die Reaktion des Methans auf Wasserdampf wird durch die Menge des Wasserdampfes wesentlich beeinflusst.

Lässt man 100 *VT* Methan mit $n \cdot 100$ *VT* Wasser nach der Gleichung $CH_4+H_2O=CO+3\ H_2$ auf einander reagieren, und setzt die verwandelte Menge des Methans gleich x, so betragen die Volumen nach Gleichungseinstellung $(100-x)\ CH_4$, $(n \cdot 100-x)\ H_2O$, x CO und $3x\ H_2$. So ergibt sich das Kp nach folgender Formel.

$$Kp_1 = \frac{(100-x)(n \cdot 100-x)\left[100(n+1)+2x\right]^2}{27x^4}$$

$$\log Kp_1 = \log(100-x)+\log(n \cdot 100-x)+2\log\left[100(n+1)+2x\right]-4\log x-1.43$$

Wenn man 100 *VT* Methan mit $2n$ 100 *VT* Wasser nach der Gleichung $CH_4+2H_2O=CO_2+4H_2$ auf einander reagieren lässt und die verwandelte Menge des Methans x stellt, so betragen die Volumen nach der Gleichungseinstellung $(100-x)CH_4$, $2(n \cdot 100-x)H_2O$, $x\ CO_2$ und $4xH_2$. So ergibt sich Kp, wie in der Formel gezeigt,

$$Kp_2 = \frac{(100-x)(n\ 100-x)^2\left[100(2n+1)+2x\right]^4}{64x^5}$$

$$\log Kp_2 = \log(100-x)+2\log(n\ 100-x)+2\log\left[100(2n+1)+2x\right]-5\log x-1.806$$

Wenn man die Werte n=1,2,3 annimt, so ergeben sich die Komponenten des Reaktionsendgases wie in Tafel 4 und 5 dargestellt. Abb. 4 und 5 zeigen die Verhältnisse zwischen dem Verwandlungsgrad des

Methans und $\log Kp$ als $n=1,2,3..$ Ein im Ueberschuss vorhandene Wasserdampf bewirkt eine Steigerung des Methanumsatzes. Man kann durch Verwendung der Abb. 2 und Abb. 4 oder Abb. 5 das Gleichgewicht des Methans unter allen Bedingungen berechnen.

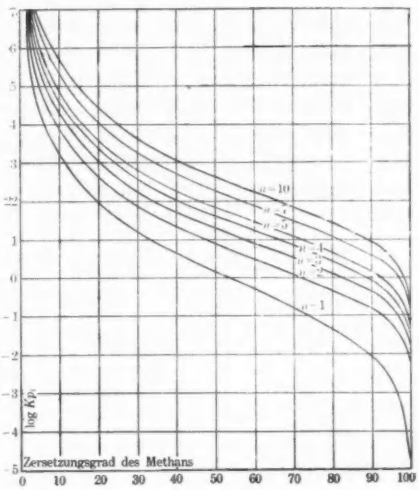

Abbildung 4.
$\log Kp_1$ und Wassermenge.

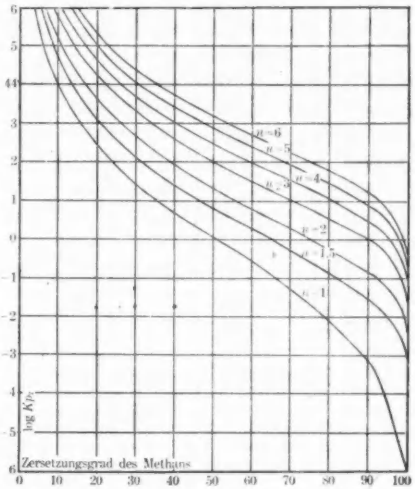

Abbildung 5.
$\log Kp_2$ und Wassermenge.

Beispiel 1. Die Temperatur, die zur 70% Veränderung des Methans mit dreimal soviel Wasserdampf der theoretischen Menge nötig ist, ergibt sich aus der Gleichung $CH_4+2H_2O=CO_2+4H_2$.

Mann kann aus dem Schnittpunkt der Kurve $n=3$ und der Kurve 70% in Abb. 5 $\log Kp_2=1.05$ feststellen. Dann erhält aus $\log Kp_2$ Kurve $t°C=545°$. Es ist die erforderliche Temperatur. Abb. 5 veranschaulicht, dass 6 facher Wasserdampf der theoretische Menge bei 545°C. 92.0% Verwandlung bewirkt.

Beispiel 2. zeigt das Verhältnis zwischen dem Verwandlungsgrade und der Wassermenge nach der Gleichung $CH_4+H_2O=CO+3H_2$ bei 800°C.

Man findet zuerst aus Abb. 2 die Werte $\log Kp=-1.90$ bei 800°C, dann aus Abb. 4 den Verwandlungsgrad 99.0% bei $n=2$, 88.5% bei $n=1$. Tafel 4 und 5 zeigen die Komponenten der Reaktionsgase bei Temperatur- und Wasserdampf-veränderung.

Tafel 4. $\log Kp_1$ und Wassermenge.

°C	$\log Kp_1$	$n=1$			$n=2$			$n=3$		
		CO	H_2	CH_4	CO	H_2	CH_4	CO	H_2	CH_4
400	4.637	3.89	11.67	84.44	5.37	16.11	78.52	6.38	19.14	74.48
450	3.367	7.09	21.27	71.64	9.35	28.05	62.60	10.95	32.85	56.20
500	2.460	10.25	30.75	59.00	12.93	38.79	48.28	16.75	50.25	33.00
550	1.508	14.38	43.14	42.48	17.30	51.90	30.80	19.00	57.00	24.00
600	0.663	17.96	53.88	28.16	20.86	62.58	16.56	22.07	66.21	11.72
650	−0.093	20.73	62.19	17.08	23.00	69.00	8.00	24.06	72.18	3.76
700	−0.773	22.57	67.71	9.72	24.24	72.72	3.04	24.67	74.01	1.32
750	−1.339	23.65	70.95	5.40	24.75	74.25	1.00	24.92	74.76	0.32
800	−1.943	24.20	72.60	3.20	24.91	74.73	0.36	24.95	74.85	0.20
850	−2.454	24.55	73.65	1.80	24.97	74.91	0.14			
900	−2.924	24.73	74.19	1.08						
950	−3.352	24.82	74.46	0.72						
1000	−3.748	24.83	74.49	0.68						
1050	−4.087	24.93	74.79	0.28						
1100	−4.456	24.96	74.88	0.16						
1150	−4.773	24.97	74.91	0.14						

Tafel 5. $\log Kp_2$ und Wassermenge.

°C	$\log Kp_2$	$n=1$			$n=1.5$			$n=2$		
		CO_2	H_2	CH_4	CO_2	H_2	CH_4	CO_2	H_2	CH_4
400	3.547	8.39	33.56	58.06	9.98	39.92	50.10	11.20	44.80	44.00
450	2.478	11.12	44.48	44.40	12.80	51.20	36.00	13.95	55.80	30.25
500	1.740	12.93	51.72	35.35	14.62	58.48	26.90	15.75	63.00	21.25
550	0.937	14.82	59.28	25.90	16.40	65.60	18.00	17.40	69.60	13.00
600	0.222	16.17	64.68	19.15	17.65	70.60	11.75	18.50	74.00	7.50
650	−0.419	17.35	69.40	13.25	18.58	74.32	7.10	19.23	76.92	3.85
700	−0.997	18.12	72.48	9.40	19.17	76.68	4.15	19.67	78.68	1.65
750	−1.524	18.62	74.48	6.90	19.58	78.32	2.10	19.87	79.48	0.65
800	−1.990	18.95	75.80	5.25	19.80	79.20	1.00	19.93	79.72	0.35
850	−2.429	19.24	76.96	3.80	19.90	79.60	0.50	19.97	79.88	0.15
900	−2.835	19.43	77.72	2.85	19.95	79.95	0.25			
950	−3.203	19.58	78.32	2.10						
1000	−3.543	19.66	78.64	1.70						
1050	−3.833	19.75	79.00	1.25						
1100	−4.159	19.76	79.04	1.20						
1150	−4.431	19.88	79.52	0.60						

Tafel 4.—(*Fort.*)

$n = 4$			$n = 5$			$n = 7$			$n = 10$		
CO	H_2	CH_4	CO	H_2	CH_4	CO	H_2	CH_4	CO	H_2	CH_4
7.52	22.56	69.92	8.21	24.63	67.16	10.00	30.00	60.00	11.43	34.29	54.28
12.25	36.75	49·00	13.37	40.11	46.52	15.30	45.90	38.80	16.83	50.49	32.68
16.22	48.66	35.12	17.38	52.14	30.48	19.13	57.39	23.48	20.62	61.86	17.52
20.27	60.81	18.92	21.16	15.36	15.36	22.53	67.59	9.88	23.54	70.62	5.84
22.24	66.72	11.04	23.43	70.29	6.28	24.23	72.69	3.08	24.58	73.74	1.68
24.33	72.99	2.68	24.55	73.65	1.80	24.84	74.52	0.64	24.90	74.70	0.40
24.88	74.64	0.48	24.90	74.70	0.40	24.96	74.88	0.16	24.98	74.94	0.08
24.96	74.88	0.16	24.97	74.91	0.14						

Tafel 5.—(*Fort.*)

$n = 3$			$n = 4$			$n = 5$			$n = 6$		
CO_2	H_2	CH_4	CO_2	H_2	CH_2	CO_2	H_2	CH_4	CO_2	H_2	CH_4
12.98	51.92	35.10	14.17	56.68	29.15	15.13	60.52	24.35	17.68	70.72	11.60
15.63	62.52	21.85	16.72	66.88	16.40	17.45	69.80	12.75	18.00	72.00	10.00
17.18	68.72	14.10	18.05	72.20	9.75	18.64	74.56	6.80	19.00	76.00	5.00
18.53	74.12	7.35	19.17	76.68	4.15	19.52	78.08	2.40	19.78	79.12	1.10
19.35	77.40	3.25	19.72	78.88	1.40	19.87	79.48	0.65	19.94	79.76	0.30
19.77	79.08	1.15	19.90	79.60	0.50	19.97	79.88	0.15	19.98	79.92	0.10
19.92	79.68	0.40	19.97	79.88	0.15						
19.97	79.88	0.15									

(*Fortsetzung folgt.*)

Naturgasforschungsinstitut
des Generalgouvernements von Taiwan.

Researches on the Chemical Reaction by Use of the Thermal Diffusion Apparatus of Clusius and Dickel. I. Thermal Polymerisation of Methane.*

By Kozo HIROTA.

(Received June 12, 1941.)

Introduction. Separation of gases by thermal diffusion method is much improved by the application of an apparatus[1], sometimes called thermal diffusion column, by means of which many researches are going on in order to separate isotopes such as those of chlorine, xenon, mercury and carbon[2], while the author has used the apparatus as a rectifying column and discussed its efficiency[3]. The author also tried to use the apparatus as a reaction vessel, intending to perform a chemical reaction smoothly and completely as well as to separate the reactants at the same time by the action of thermosyphone found by Clusius and Dickel.

Object of the Research. On the first trial, the thermal polymerisation (or cracking-polymerisation) of methane,

$$CH_4 \rightarrow H_2 + \text{Higher Hydrocarbons},$$

which was found in nineteenth century and was extensively studied by F. Fischer[4] in 1928, was carried out, because the effect would be remarkable in this reaction for the following reason, and on the other hand this reaction is important from the industrial point of view.

The elementary process of the above reaction is considered, at present,[4][5] though not yet definitely determined in detail, to consist in two stages: the first stage in which methane is cracked in hydrogen and some free radicals* and the second stage in which these free radicals polymerise into higher hydrocarbons, such as benzene and naphtalene. At high temperatures at which the reaction takes place with a measurable speed, both free radicals and hydrocarbons produced are very unstable and decompose easily into hydrogen and elementary carbon.

$$\begin{array}{ccc} & CH_4 \rightarrow H_2 + \text{Free Radicals} & \\ & \swarrow \quad \searrow & \\ \text{Elementary Carbon} + H_2 & & \text{Higher Hydrocarbons} + H_2 \end{array}$$

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* Main part of this paper was read at the annual meeting of the Chemical Society of Japan (April 5, 1941).

(1) K. Clusius and G. Dickel, *Naturwissenschaften*, **26** (1938), 546.

(2) For instance, a) Cl, K. Clusius and G. Dickel, *ibid.*, **27** (1939), 148, 487; b) Xe, W. Groth, *ibid.*, 260; c) Hg, W. Groth and P. Harteck, *ibid.*, 584; d) C, H. S. Taylor, *Nature*, **144** (1939), 8.

(3) K. Hirota, *J. Soc. Chem. Ind. Japan*, **44** (1941), 391.

(4) F. Fischer, *Brennstoff Chem.*, **9** (1928), 308.

(5) H. M. Stanley and W. Nash, *J. Chem. Soc. Ind.*, **48** (1928), 1.

* The kind of free radicals is considered as CH_3, CH_2 or CH, according to the different theory, but is not the main point of the argument.

So the important condition in getting a yield of hydrocarbons is to prevent the decomposition of free radicals in the hot region and to make those polymerise in the cold region. To meet this, Fischer passed methane very rapidly through a porcelain or quartz tube laid horizontally and heated at 900°C. or above, but his maximum yield of condensed hydrocarbons is 0.126 g. per liter of methane[4][6], i.e., the conversion of 18% of the original methane. Kobayashi and others[7] modified the method so as to pass the cracked methane through a slightly colder tube in order to acceralate the polymerisation of the free radicals. Dilution of the methane with nitrogen, hydrogen, chlorine, water steam or other gases[8] cannot alter the yield considerably better and rather unfavourably in some cases. Hessel and others[9] used a vertical tube and mixed some gaseous hydrocarbons or chlorine gas into the original methane. All these results obtained with a quartz and a porcelain tube, however, are of the same degree as some of these are shown in Table 1, while it was found that metallic tubes are not suitable on account of its catalytic power of accerelating the decomposition into carbon and hydrogen.

Table 1. Maximum Yield of Condensed Hydrocarbons in the Reaction, $CH_4 \rightarrow H_2$ + Higher Hydrocarbons.*)

Investigators	Vol. % of CH_4 in original gas	Conditions		Condensed Hydrocarbons		
		Temp. (°C.)	Contact Time(sec.)	Light Oil (g./l.)	Tar (g./l.)	Total (g./l.)
Fischer[4]	93	1050	—	0.009	0.0045	0.014
Stanley, Nasch[5]	93	1150	0.6	0.028	0.035	0.063
Fischer, Pichler[6]	—	1300	0.016	0.050 (0.110)	0.076 (0.082)	0.126 (0.192)
Oda[10]	82	1200	0.23	0.026 c.c./l.	0.023	—
Kobayashi, etc.[7]	76	1100	0.45	0.091	0.022	0.113
Hessel, etc.[9]	—	1190	0.29	0.031 (0.117)	0.029 (0.115)	0.050 (0.232)

Now if the reaction is carried on in the thermal diffusion column, we can consider that it will proceed as follows:—

Methane gas, introduced in from the bottom of the column, is cracked into hydrogen gas and free radicals at the electrically heated wire, placed in the central axis of the column. By the action of thermosyphone, the hydrogen molecules, the molecular weight of which is small, rise up along the heated wire and flow out from the top of the column, while the free

(6) F. Fischer and H. Pickler, *Brennstoff Chem.*, **13** (1932), 381.
(7) K. Kobayashi, K. Yamamoto, H. Ishikawa and S. Hinonishi, *J. Soc. Chem. Ind. Japan*, **37** (1937), 785.
(8) G. Egloff, "The Reaction of Pure Hydrocarbons", 64 (1937).
(9) W. Hessels, D. W. von Krevelen and H. I. Waterman, *J. Soc. Chem. Ind.*, **58** (1939), 321.
* Values in parenthses are obtained by repeated treatment of the gas for four times.

radicals go down along the cold wall, polymerising into higher hydrocarbons. Then we can expect in this process (i) that the decomposition of free radicals and higher hydrocarbons diminishes and (ii) that the reaction takes place completely, because the unreacted methane remains in the column, repeatedly colliding with the wire.

Experiment. The experiments were carried out at one atmospheric pressure. The column was a boron-glass (terex glass) tube of 1.01 meter in length and of 2.0 cm. in diameter with a tungsten wire of 0.75 mm. in diameter and 70 cm. in length and with a cooling glass tube of running water. Methane gas was prepared from sodium acetate and soda lime in an ordinary way. A gas interferometer was used constantly throughout the experiments for the check of gas analysis. Other details of the experimental procedures have been described in anothr journal[11], so only the summarised results are shown in Table 2 and 3.

Table 2. Summarised Experimental Results I.

No. of Exp.	Original Gas		Experimental Conditions				
	Vol. % of CH_4	Vol. % of H.H.C.*	Gas Vol. Used (l.)	Flow Velocity (l./hr.)	Maximum† Temp of the Wire °C.	Temp. of the Cold Wall °C.	Drying Substance
A	90	0.0	2.3	1.3	1200	34	Soda lime
B	89	0.2	7.6	6.8	1300	42	
C**	89	1.2	4.5	6.3	1200	28	
D	93	1.2	1.8	1.3	1300	30	One normal sodium hydro-oxide
E	93	1.2	3.0	1.2	1200	31	
F	93	1.2	1.9	0 4	1300	44	
G	93	1.2	2.2	0.8	1200	30	
H***	93	1.2	5	3.0	1300	35	

† Maximum Temp. of the Wire was obtained pyroptically. This value was probably too low on account of the disturbance caused by a brown product deposited on the cold glass wall.

* H. H. C. means heavy hydrocarbons.

** Part of the reacted gas was let to flow out from the bottom of the column too with the flow velocity of 0.2 liter per hour, and had the composition as follows: CH_4 91%, H_2 2%, etc.

*** Tungsten wire coated with sodium silicate was used.

(10) R. Oda, *J. Soc. Chem. Ind. Japan*, **37** (1934), B 630.

(11) K. Hirota, *J. Chem. Soc. Japan*, (Printed in Japanese) **62**, (1941), 392.

In the course of these experiments upper part of the wire was observed to be less bright than the lower part, probably owing to the higher concentration of hydrogen as would be expected.

Table 3. Summarised Experimental Results II.

No. of Exp.	Produced Gas				Produced Hydrocarbons			
	Flow Velocity l./hr.	Expansion Ratio	Vol. % of H_2	Vol. % of CH_4	Liqiud (g./l.)	Solid (g./l.)	Total (g./l.)	Ratio
A	0.6	0.5	77	11	0.12	0.04	0.16	3
B	3.7	0.5	79	11	0.03	0.02	0.05	1.5
C	4	0.6	33	59	0.09	>0.005	0.09	<20
D	1.6	1.2	87	6	0.22	0.08	0.30	3
E	1.6	1.3	82	12	0.14	0.01	0.15	14
F	0.4	1.0	80	14	0.10	0.05	0.15	2
G	0.3	0.4	85*	—	0.17	0.07	0.24	3
H	2.0	0.6	60*	—	0.00	0.08	0.08	∞

* These values were estimated from the refractive index of the gas produced.

Discussion. I. The maximum yield of condensed hydrocarbons was 0.30 g. per liter of the original methane used, i.e., the conversion of 42%, and the concentration of hydrogen in the reacted gas amounted to 87% in the same experiment. This results are much superior to those of the researches of other investigators, and, moreover, to those obtained after the treatment of four times[6]-[8].

II. Experiment H seems to show that a surface covered with non-metallic substance favours the undesirable decomposition to carbon and hydrogen, in spite of the reversed result of other investigators, but this might be due to the fact that contact plane of the wire to gas could not be heated fully.

III.(*) From the above experiments the following relations could be deduced easily:—

(i) Comparing A and B to D, E, F and G, small degree of drying seems to act to prevent the decomposition into carbon and hydrogen as indicated in the expansion ratio.

(ii) Comparing D to E, higher temperature seems to act to decrease the ratio of the liquid to the solid product and to increase the total yield.

(iii) The effect of flow velocity exists, if D to F is compared.

But as the number of the experiments is small, it must be examined carefully by later researches if these relations really hold.

IV. The liquid and solid products had the odour of toluene and naphtalene respectively. Both were insoluble in water and liquid paraffine and were hardly soluble in ethyl alcohol but soluble in benzene. These materials could be considered to be higher aromatic hydrocarbons. This conforms with the previous researches in connecton with this point.

* Content of this paragraph is slightly different from that in ref. (11) on account of the addition of new data.

As it has been shown very effective to use a thermal diffusion apparatus of Clusius and Dickel as a reaction vessel, the author is going not only to study the reaction expensively, but also to apply the method to other reactions.

Summary.

(1) A method of thermal polymerisation of methane proceeding in a thermal diffusion column of Clusius and Dickel has been described and discussed.

(2) By this method a good yield of condensed hydrocarbons and highly concentrated hydrogen gas have been obtained.

(3) Effects of the experimental conditions have been obtained.

In conclusion the author wishes to express his sincere thanks to Dr. R. Yoshimura, Director of the Department, for his interest and encouragement in carrying out this research.

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The Separation of Iso- and Normal Butyl Alcohols from Hydrocarbons by Azeotropic Distillation.

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(Received June 17, 1941.)

Two of the promising methods of the synthesis of iso- and normal butyl alcohols are first, the reaction of a mixture of hydrogen and carbon monoxide[1-5] under pressure in the presence of a suitable catalyst and, second, dehydration and polymerization of the lower alcohols[6-8] under ordinary or elevated pressures in the presence of a catalyst. By either method, the products are not pure iso- and normal alcohols, but contain

(1) G. T. Morgan, R. Taylor, and T. J. Hedley, *J. Soc. Chem. Ind.*, **47** (1928), 117T; R. Taylor, *J. Chem. Soc.*, **1934**, 1429; G. T. Morgan, Hardy, and Proctor, *J. Soc. Chem. Ind.*, **51** (1932), 1T; G. T. Morgan and R. Taylor, *Proc. Roy. Soc.*, A **131** (1931), 533.

(2) G. Natta, *Osterr. chem. Zeitg.*, **40** (1937), 162.

(3) E. M. Bocharova, B. N. Dolgov, and Z. M. Prokhorova, *Khim. Tverdogo Topliva*, **6** (1935), 665; *Chem. Abst.*, **30** (1936), 2171.

(4) I. G. Farbenind., A. G., G. P. 625757 (1936).

(5) H. Tahara, Y. Tatuki, and J. Simizu, *J. Soc. Chem. Ind., Japan* (Supp. Binding), **43** (1940), 82.

(6) Neuman, Brit. P. 326812 (1923).

(7) O. Fuchs and W. Querfurth, G. P. 594672; U. S. 205078.

(8) Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, G. P. 674751 (1939); Brit. P. 478141 (1938).

a large number of hydrocarbons. Ordinarily, the alcohols are separated by distillation because of convenience and simplicity. However, owing to the circumstance that the alcohols are susceptible to the formation of azeotropic mixtures with a large number of hydrocarbons, straight forward distillation cannot be expected to give accurate results. Because of the fact that the alcohols form also azeotropic mixtures with water, distillation method can be so modified, taking advantage of the fact, to give a convenient and accurate separation of the alcohols from the hydrocarbons.

The purpose of this paper is to describe this method in some detail and to give the experimental results obtained from the measurements of alcohol-toluene and alcohol-gasoline mixtures. We have assumed in our case that the only water soluble substances are the alcohols. The separation of the alcohols from the mixtures containing such oxygenated compounds as the lower alcohols, aldehydes, and ketones, besides hydrocarbons will be the subject of a subsequent report, which will appear later in this bulletin.

In the present method, the following properties of the alcohols have been taken advantage of:

(1) The alcohols dissolve appreciably[9] (at 20°C. the normal dissolves 7.8% and the iso- 8.5% by weight) in water, while hydrocarbons do not[10].

(2) The alcohols dissolve completely in ether, while water does not but slightly.

(3) The alcohols form azeotropic mixtures with water, but not with ether.

Experimental Details.

A) **Purification.** *Normal Butyl Alcohol.* It was purified by a method similar to that given by Weissberger and Proskauer[11]. It was washed with dilute sulphuric acid and then with sodium bisulphite. Then it was boiled with an aqueous KOH solution. A boiling fraction, 116.5–118°C., was first collected, and the final distillation was made over CaO. A fraction boiling at 117–118°C. was used.

Iso-Butyl Alcohol. A commercial product was first treated with quick lime and then distilled. A fraction boiling between 106.9–108.5 was collected.[12]

Toluene. It was purified[13] by washing with concentrated H_2SO_4 and with water. It was then dried over $CaCl_2$, and the final distillation was made over metallic sodium. A fraction boiling at 110–112°C. was collected.

Gasoline. Commercial gasoline[*] was purified by treating it with con-

(9) A. Seidell, "Solubility of Inorganic and Organic Compounds," D. Van Nostrand Co., Vol. II, 1121 (1928).

(10) Int. Crit. Tables, III, 387 (1928). Dissolves but slightly.

(11) A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Press, 126 (1935).

(12) Kuwada, "Solvents," Maruzen, 219 (1940). In Japanese.

(13) G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7** (1939), 1087.

* "Rising Sun," brand, straight-run.

centrated H_2SO_4, KOH, H_2O, dried with $CaCl_2$, and finally distilled over metallic sodium. Fractions boiling from 50 to 130°C. were used.

Ether. It was first treated[14] with concentrated sulphuric acid and then washed with KOH and water. It was then distilled over metallic sodium. A fraction, 36.0–37.0°C. was used.

B) **Method.** No special apparatus was used. 500 c.c. and 100 c.c. (for ether extractions) separatory flasks; calibrated 30 c.c. graduated cylinders, which were graduated to 0.1 c.c., with well-fitting ground glass stoppers; and a distillation set-up made of Terex glass with interchangeable ground glass joints were used. The distillation column was insulated by an annular space of air formed by fitting a glass tube over its whole length. The column was about 60 cm. in length and contained a Terex glass spiral. Heating was made either electrically or by gas. The temperature was measured by means of an alumel-chromel thermocouple connected to a potentiometer whose scale readings could be estimated to about 0.2°C.

The alcohols were first separated from the hydrocarbons by adding water 20 times[15] the volume of the sample and shaken and left alone until all the alcohols had separated out from the hydrocarbon phase. It was shown by the results of Table 1 that 1.5 hours were sufficient to separate toluene completely (and also the alcohols; compare the results of Table 2) from the mixture. In order to break up the last traces of the emulsion formed by the system, the mixture was heated at 60°C. As it was indicated by the Table, 50°C. seemed not sufficient, and at this temperature the time of heating had to be longer. One shaking was adequate to remove practically all of the alcohols. The non-dissolving fraction was considered hydrocarbons. The validity of this assumption is justified, as shown by the results of Tables 1, 2, and 3.

To extract and concentrate the alcohols from such dilute aqueous solutions by means of some selective solvent appears unnecessarily tedious and wasteful in view of the fact that iso- and normal butyl alcohols form azeotropic mixtures with water in the respective proportions[16] (by weight of alcohol), 67% and 57.6%, at the constant boiling points[16], 90.0 and 92.6°C., respectively.

Distillations were carried out in the apparatus, which has been mentioned above. Until the last traces of the alcohol had disappeared, the boiling point was constant; moreover, the distillation could be made quite rapidly and roughly without fear of introducing serious errors. It was continued until 100°C.[17]. When it was completed, the distillates, which had separated out into two layers, were shaken to bring about an equilibrium between alcohol and water, and the respective amounts of the alcohol in the water and the water in the alcoholic phase were corrected for at the experimental temperature. The above method was sufficient to determine accurately the amounts of the alcohols in their binary systems

(14) C. W. Porter, T. D. Stewart, and G. E. K. Branch, "Methods of Organic Chemistry," Ginn and Co., 70 (1927).

(15) V. G. Shaposhnikov and S. E. Pinchuk, *Chem. Abst.*, **30** (1936), 4787. They have suggested 35 fold addition in a similar separation.

(16) T. H. Durrans, "Solvents," Chapman and Hall, 102, 103 (1938).

(17) By 95°C practically all of the alcohols had been distilled out.

Table 1. Effects on Separation of Toluene of Time and Temperature.

Toluene-Iso alcohol Systems.*

Time left alone after shaking (hr.)	Conditions of aqueous layer	Temp. °C. of destroying emulsion	Time of heating (min.)	Toluene (c.c.)	Recovery %
1.0	Not quite clear	70	6	9.66	3.4
1.5	Clear	60	8	9.76	2.4
2.0	Clear	60	7	9.73	2.7
3.0	Clear	50	16*	9.71	2.9
4.0	Clear	60	6	9.75	2.5

* Break-up appeared not quite complete.

Toluene-Normal alcohol Systems.**

Time left alone after shaking (hr.)	Conditions of aqueous layer	Temp. °C. of destroying emulsion	Time of heating (min.)	Toluene (c.c.)	Recovery %
1.0	Not quite clear	60	9	9.64	3.6
1.5	Clear	60	7	9.72	2.8
2.0	Clear	60	6	9.80	2.0
3.0	Clear	60	5	9.79	2.1

** Conditions: toluene 10 c.c.; alcohol 10 c.c.; water 400 c.c.; time of shaking 5 minutes.

with hydrocarbons. If, however, a system contains both alcohols and hydrocarbons simultaneously, several additional steps must be made in order to separate the respective alcohols from each other. These additional operations involve, first, the extraction with ether[5] of the alcohols from the aqueous phase and, second, the separation of the alcohols by distillation.

Results. The simpler method has been used for the separation of iso- and normal alcohols from their respective binary systems with toluene, and the results obtained at 15°C. (unless otherwise stated) are shown in Table 2. The actual amounts of toluene and the alcohols lost are independent of the amounts of the respective components in the system. What this means is, among others, that the loss is mainly operational. The results of our measurements indicate that the method is quite simple and fairly accurate. At present, we do not have a suitable explanation of the fact that the loss of toluene in the normal system is consistently smaller than that in the iso- system.

For the mixtures consisting of iso-, normal butyl alcohols, and commercial gasoline, the more involved method was used. The alcohols were separated from the gasoline and concentrated as in the simpler method.

Then to the distillates a sufficient amount of $CaCl_2$ was added to saturate the aqueous phase. Then by four separate additions of the same volume as that of the distillates of ether, the alcohols were completely extracted from water. Ether and the alcohols were, then, separated from each other by distillation which presented no difficulty.

Table 2.

Normal Butyl Alcohol-Toluene Systems at 15°C.

Vol. c.c.		Toluene c.c.		Alcohol recovered c.c.				% Alcohol Loss
Alcohol	Toluene	Recov.	Loss	Alc. phase	Aqueous phase	Total	Loss	
5*	15	14.83	0.17	4.04	0.67	4.71	0.29	5.8
5*	15	14.83	0.17	3.54	1.21	4.76	0.24	4.8
10	10	9.72	0.28	8.73	1.13	9.86	0.14	1.4
10	10	9.77	0.23	9.04	0.79	9.83	0.17	1.7
15*	5	4.76	0.24	12.64	2.03	14.71	0.29	1.9
15*	5	4.83	0.17	12.37	2.35	14.72	0.28	1.9

* At 10°C.

Iso-butyl Alcohol-Toluene Systems.

Component c.c.		Toluene c.c.		Alcohol Recovered c.c.				% Alcohol Loss
Alcohol	Toluene	Recov.	Loss	Alc. phase	Aqueous phase	Total	Loss	
5	15	14.75	0.25	4.66	0.33	4.99	0.01	0.2
5	15	14.77	0.23	4.49	0.45	4.94	0.06	1.2
10	10	9.72	0.28	8.65	1.08	9.82	0.28	2.8
10	10	9.73	0.27	8.85	0.84	9.68	0.32	3.2
15	5	4.78	0.22	14.29	0.68	14.97	0.03	0.2
15	5	4.73	0.27	13.95	0.89	14.84	0.16	1.1

The iso-butyl alcohol range was taken from 100 to 111°C., and what had been left over undistilled was considered all normal alcohol. As indicated by Fig. 1 and Table 3, the separation of iso-butyl alcohol is complete, and although a range from 100 to 111°C. has been taken, in reality, practically all has come out at a constant temperature, 108.4°C. The range of temperature, 100 to 108°C., is due to the time lag in bringing the thermocouple to the proper temperature.

As can be seen from Table 3, the actual loss in c.c. of the gasoline is about the same in each run, but it is larger than that of toluene. This is probably due to a higher volatility of the gasoline. Regardless of the amounts of the individual alcohols, the loss in each run is about the same; moreover, it is of the same order of magnitude as that in the toluene-alcohol systems. This indicates that the loss is, as it has been already

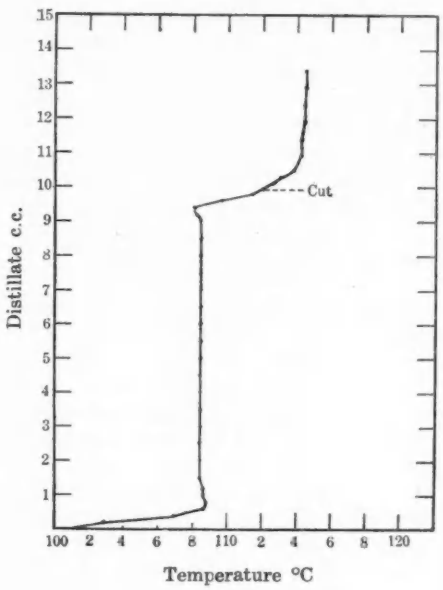

Fig. 1.

mentioned, chiefly mechanical. When the results of the two tables are compared, some information as to the sources of error involved in the present method may be gained. In Table 3 the amounts of iso- and of normal alcohols finally separated are always less than the original amounts and they are about the same as those in Table 2. What it means is that during the ether extractions and the final distillation the loss is negligible, and the main source of error seems either in the extraction by water of the alcohols or in the distillation of the azeotropic mixtures. By a number of preliminary runs the latter has been shown to give negligible error; therefore the chief source must be the former. The same inference can be drawn

Table 3.

Iso- and Normal Butyl Alcohols-Gasoline Systems at 15°C.

Components c.c.			Gasoline c.c.			Iso-Alcohol c.c.			Normal Alcohol c.c.		
Gasoline	Iso-	Normal	Recov.	Loss	% loss	Recov.	Loss	% loss	Recov.	Loss	% loss
10	10	10	9.64	0.36	3.6	9.70	0.3	3.0	9.67	0.33	3.3
10	10	10	9.67	0.33	3.3	9.75	0.25	2.5	9.73	0.27	2.7
10	10	10	9.64	0.36	3.6	9.80	0.20	2.0	9.68	0.32	3.2
10	5	15	9.60	0.40	4.0	4.83	0.17	3.4	14.91	0.09	0.6
10	15	5	9.52	0.48	4.8	14.78	0.22	1.4	4.75	0.25	5.0

from the fact that some difficulties, which have been already referred to, are encountered with in connection with the extraction.

Finally, a word may be mentioned of the accuracy of the method. Since the actual loss is independent of the total amount of each component in the system, the larger the amount of the component, the smaller will be its percentage error. If the alcohol to be separated is about 5 c.c., the percentage error is about 5; for 10 c.c., it is about 3%; and for over 15 c.c., it can be reduced to about 1%.

Summary.

A new method has been devised, employing the principle of azeotropic distillation, to separate iso- and normal butyl alcohols from hydrocarbons.

This method has been applied to the binary systems of iso- and normal alcohols with toluene. It has also been tried with the mixtures of the alcohols and gasoline. The individual components have been separated, and it has been shown that this method is accurate within 5% when the amount of the component to be separated is about 5 c.c.; 3% when it is 10 c.c.; and about 1% or less for the amount larger than 15 c.c.

The authors are grateful to Dr. Sato, the director of the institute, for permitting us to publish this paper.

The Central Laboratory,
South Manchuria Railway Company,
Dairen, Japan.

Über die Bildung der partiellen Acetate von Flavonen, Flavanonen, Anthrachinonen und dergleichen Verbindungen.

Von Masami SIMOKORIYAMA.

(Eingegangen am 2. Juli 1941.)

Bei der Methylierung von Flavonen, Flavanonen, Anthrachinonen und dergleichen Verbindungen, namentlich im Falle mit Diazomethan, stiessen wir gewöhnlich auf nicht kleinen Widerstand des der Carbonylgruppe ortho-ständigen Hydroxyls. Dies sollte, wie allegemein anerkannt, auf der Chelatbildung zwischen der letzteren Gruppe mit der ersteren beruhen. Falls diese von vielen Seiten vertretene Ansicht zutrifft, so müsste sich die Reaktionsträgheit der betreffenden Hydroxylgruppe auch bei Acetylierung geltend machen. In dieser Hinsicht untersuchte ich über das Verhalten von Substanzen oben genannter Stoffklasse in dem unter milden Bedingungen ausgeführten Acetylierungsverfahren, und fand, dass sie Acetate gaben, welche gegen Eisen(III)chlorid ausgezeichnete purpurbraune Farbreaktion zeigten. Wider Erwarten bildeten dabei jedoch *o*-Oxybenzoesäuren Ausnahmen, welche ohne Schwierigkeit vollständig acetylierte Derivate lieferten. Was die Ursache hierfür sei, ist mir zur Zeit unbekannt. Wohl ist die Chelatbildung in diesen Fällen viel lockerer.

Um den Essigsäurerest einzuführen, kann man sich natürlich über verschiedene Acetylierungsmethoden verfügen. Man acetyliert bisweilen in Gegenwart etwaigen indifferenten Verdünnungsmittels oder meistens ohne Verdünnungsmittel, d. h. durch unmittelbares Zusammenbringen der zu acetylierenden Substanz mit dem Acetyliermittel, z. B. Essigsäureanhydrid, ausführen, wobei die Reaktion in der Kälte nur langsam vor

sich geht. So ist dazu meist mehrstündiges Erwärmen in Anspruch genommen. Natürlich verläuft die Acetylierung glatt, wenn man eine kleine Menge Reaktionsbeschleuniger, wie z. B. konzentrierte Schwefelsäure[1], Natriumacetat[2] oder Pyridin[3], u. a. hinzufügt.

Den Zusatz von Pyridin bei Acetylierungen mittels Essigsäureanhydrids haben R. Behrend und P. Roth[3] im Jahre 1904 zuerst für die Herstellung von Zuckeracetaten vorgeschlagen und diese Methode wurde nachher von E. Fischer und M. Bergmann[4] als den mildesten Weg der Acetylierung empfohlen.

Ich bediente mich in vorliegender Untersuchung auch der oben erwähnten Pyridinmethode, in welcher aber das Pyridin nur im Sinne eines Katalysators[5], nämlich in sehr kleiner Menge, verwendet wird.

Zur Untersuchung dienten einfache *o*-Oxyphenyl-aldehyde, -ketone u. -säuren, *o*-Oxy-flavone, -flavanone und -anthrachinone. Alle zur Untersuchung verwendeten Substanzen wurden in einem kleinen Röhrchen, den Zahlen der Hydroxylgruppen entsprechend, mit ca. 5–10 Mol. Essigsäureanhydrid gemischt, mit 2–3 Tropfen Pyridin versetzt und das Gemisch mit Glasstab gut umgerührt, wobei die Reaktion, mit schwacher Wärmeentwicklung begleitet, spontan vor sich geht, indem es sich entweder eine klare Lösung bildet oder Krystalle des Acetates sich ausscheiden und der Inhalt eventuell zu einer breiigen Masse erstarrt, je nachdem das gebildete Acetat in Essigsäure-anhydrid leicht löslich ist oder schwer bzw. unlöslich ist. Im grossen und ganzen vollzieht sich die Reaktion innerhalb 2–3 Minuten. Dann wird das Gemisch mit Wasser versetzt und die abgeschiedene Reaktionsmasse abfiltriert, mit Wasser gut gewaschen und aus geeignetem Lösungsmittel umkrystallisiert. Auf diesem Wege kann man schon hinreichend reines Acetat in krystallisierter Form gewinnen. Durch diese Methode erhielt ich bei Verbindungen, welche nicht dem Carbonyl *o*-ständige Hydroxylgruppe tragen, Peracetate (Phloroglucin, Pyrogallol, Fisetin und ausnahmsweise Salicylsäure, β-Resorcylsäure, Brenzcatechin- und Pyrogallol-*o*-carbonsäure) und von solcher, welche u. a. dem Carbonyl *o*-ständige Hydroxylgruppe trägt, Acetat, in welchem die betreffende Hydroxylgruppe frei bleibt, worüber die purpurbraune Eisenchlorid-reaktion schon kundgibt.

Die so erhaltenen Acetylverbindungen werden im Vergleich mit Peracetaten in der folgenden Tabelle übersichtlich zusammengestellt.

1.	Phloroglucin	Triacetat	103–104° (104–106°[6]).
2.	Pyrogallol	Triacetat	162–163° (165°[7]).
3.	Fisetin	Tetracetat	198–200° (196–199°[8], 200–201°[9]).

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(2) C. Liebermann u. O. Hörmann, *Ber.*, **11** (1878), 1619.

(3) R. Behrend u. P. Roth, *Ann.*, **331** (1904), 362; A. Verley u. Fr. Bölsing, *Ber.*, **34** (1901), 3354.

(4) E. Fischer u. M. Bergmann, *Ber.*, **50** (1917), 1048.

(5) R. Robinson u. K. Venkataraman, *J. Chem. Soc.*, **1926**, 2347.

(6) J. Herzig, *Monatsh. Chem.*, **6** (1885), 888.

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4.	Phloroglucinaldehyd	Triacetat	122–123°[10],	Diacetat	93–94°.
5.	Resacetophenon	Diacetat	38°[11],	Monoacetat	72–73° (72°[12], 74°[13]).
6.	Gallacetophenon	Triacetat	83°[14], 85°[15],	Diacetat	78–81°.
7.	Isosakuranetin	Diacetat	138–140°,	Monoacetat	173–175°.
8.	Hesperetin	Triacetat	80–82°[16],	Diacetat	103–105°.
9.	Chrysin	Diacetat	185°[17], 192°[18], 192–194°[19],	Monoacetat	160–165°.
10.	Apigenin	Triacetat	181–182°[20],	Diacetat	192–193°.
11.	Acacetin	Diacetat	198–200°[21], 203°[22],	Monoacetat	203–208°.
12.	Baicalein	Triacetat	191–192°[23],	Diacetat	194°.
13.	Wogonin	Diacetat	152–153°[24],	Monoacetat	159–161°.
14.	Kämpferol	Tetracetat	181–182°[25],	Triacetat	177°
15.	Quercetin	Pentacetat	193–194°[26],	Tetracetat	160–162°.
16.	Myricetin	Hexacetat	214–216°[27],	Pentacetat	189–190°.
17.	Purpurin	Triacetat	200–201°[28],	Diacetat	175–178°.

18.	Salicylsäure	Monoacetat	134–135°	(135°[29], 136–137°[30]).
19.	Brenzcatechin-*o*-carbonsäure	Diacetat	146–170°	(148–150°[31]).
20.	*β*-Resorcylsäure	Diacetat	136–137°	(136–138°[32]).
21.	Pyrogallol-*o*-carbonsäure	Triacetat	163–164°	(164°[33]).

An dieser Stelle spreche ich meinem verehrten Lehrer, Herrn Prof. Dr. Sh. Hattori, meinen besten Dank für seine stetige Belehrung aus. Auch Herrn Dr. K. Hayashi des Iwata Institutes für Pflanzenbiochemie sage ich meinen besten Dank für sein liebenswürdiges Entgegenkommen zu dieser Arbeit aus.

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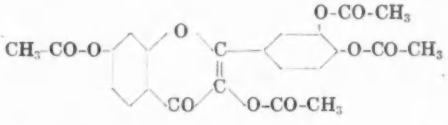
Experimenteller Teil.

1. Phloroglucin-triacetat, $C_6H_3(O{\cdot}CO{\cdot}CH_3)_3^{1,3,5}$. 0.5 g. Phloroglucin werden mit 2 ccm (5 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin versetzt. Nach ca. 1 Min. entsteht eine klare Lösung unter spontaner Temperaturerhöhung. Bald erstarrt das Ganze zu einer Krystallmasse. Phloroglucin-triacetat bildet lange weisse Nadeln aus 90-proz. Alkohol. Leicht löslich in heissem 90-proz. Alkohol. Schmp. 103–104°C. Ausbeute ca. 0.9 g.

2. Pyrogallol-triacetat, $C_6H_3(O{\cdot}CO{\cdot}CH_3)_3^{1,2,3}$. 0.5 g Pyrogallol werden in 2 ccm (5 Mol.) Essigsäure-anhydrid gelöst und dazu 2–3 Tropfen Pyridin hinzugesetzt. Nach starker Wärmeentwicklung erstarrt die Reaktionsmasse zu einem Krystallbrei, welcher nach ca. 10 Min. Stehenlassen mit Wasser versetzt wird. Das ausgeschiedene wird abfiltriert und aus 90-proz. Alkohol umkrystallisiert. Farblose kurze Prismen vom Schmp. 162–163°C. Ausbeute ca. 0.9 g.

3. Fisetin-3.7.3′.4′-tetracetat, $C_{23}H_{18}O_{10}$. 0.2 g (1 Mol.) Fisetin werden mit 0.6 ccm. (10 Mol.) Essigsäureanhydrid und 2–3 Tropfen Pyridin versetzt und mit Glasstab gut umgerührt. Nach ca. 1.5–2 Minuten beginnt die Reaktion mit schwacher Wärmeentwicklung und beendigt sich in ca. 5 Minuten. Die nun farblos gewordene Reaktionsmasse wird mit Wasser versetzt, die weisse Acetylverbindung abgesaugt, mit Wasser gewaschen und aus 90-proz. Alkohol umgelöst. Farblose Nadeln vom Schmp. 198–200°C. Schwer löslich in kaltem Alkohol, nicht so leicht löslich in heissem Alkohol. Ausbeute etwa 0.25 g.



4. Phloroglucinaldehyd-2.4-diacetat, $C_6H_2(OH)(O{\cdot}CO{\cdot}CH_3)_2{-}CHO^{1,3,5,2}$. 0.2 g Phloroglucinaldehyd (1 Mol.) werden mit 0.65 ccm. (5 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin versetzt. In ca. 1–1.5 Min. kommt die Reaktion zum Abschluss, um unter Wärmeentwicklung klare Lösung zu geben. Man versetzt mit Wasser und krystallisiert den bald erstarrenden Niederschlag aus 90-proz. Alkohol um. Weisse Nadeln vom Schmp. 93–94°C. Ausbeute ca. 0.2 g.

Gef.: C 55.43, 55.88; H 4.27, 4.53. Ber. für $C_{11}H_{10}O_6$: C 55.48; H 4.23%.

5. Resacetophenon-4-monoacetat, $C_6H_3(OH)(O{\cdot}CO{\cdot}CH_3){\cdot}CO{\cdot}CH_3^{1,3,6}$. Man erhält diese Verbindung, welche schon 1881 von M. Nencki und N. Sieber[12] und A. Michael und G. M. Palmer[13] aus Resacetophenon (1 Gew.-Tl.) durch eine Stunde langes Kochen am Rückflusskühler mit Essigsäure-anhydrid (3 Gew.-Tl.) und darauffolgende Destillation (Sdp. 303°C.) in der Vorlage krystallinisch (Schmp. 72°C.) erhalten wurde, wenn man 0.2 g. Resacetophenon (1 Mol.) in einem kleinen Röhrchen mit 0.7 ccm. Essigsäure-anhydrid (10 Mol.) und 2–3 Tropfen Pyridin versetzt und mit Glasstab umrührt. Mit schwacher Wärmeentwicklung beendigt sich die Reaktion in 2–3 Minuten. Dann versetzt man die Lösung mit Wasser und krystallisiert die entstehende farblose Krystallmasse aus verd. Alkohol um. Schmp 72–73°C. Ausbeute 0.15 g. Die alkoholische Lösung gibt mit Ferrichlorid eine purpurbraune Färbung.

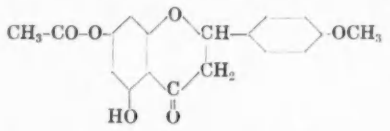
Gef.: C 61.72; H 5.36. Ber. für $C_{10}H_{10}O_4$: C 61.84; H 5.19%.

6. Gallacetophenon-3.4-diacetat, $C_6H_2(OH)(O{\cdot}CO{\cdot}CH_3)_2{\cdot}CO{\cdot}CH_3^{1,2,3,6}$. Man versetzt 0.2 g. (1 Mol.) Gallacetophenon, gelöst in 0.6 ccm. Essigsäure-anhydrid (5 Mol.), mit 2–3 Tropfen Pyridin in einem kleinen Röhrchen und rührt mit Glasstab um. In 0.5–1 Min. ist die Reaktion beendigt und eine klare gelbe Lösung ergibt sich. Nach ca. 5–10 Min. Stehengelassen, versetzt man mit Wasser und krystallisiert die schwierig erstarrende gelbbraune Reaktionsmasse aus verd. Alkohol um. Schmp.

78–81°C. Die alkoholische Lösung gibt mit Ferrichlorid eine purpurbraune Färbung. Diese Substanz ist nicht mit der Verbindung identisch, welche von G. Heller[34] aus Pyrogallol-triacetat durch halbstündiges Erhitzen mit $ZnCl_2$ auf 130–135°C. erhalten wurde. Sie zeigte nach dem Umkrystallisieren aus Eisessig den Schmp. 217–219°C. und gab mit Ferrichlorid eine dunkelrote Färbung.

Gef.: C 56.68; H 4.37. Ber. für $C_{12}H_{12}O_6$: C 57.14; H 4.76%.

7. Isosakuranetin-7-monoacetat, $C_{18}H_{16}O_6$. Versetzt man 0.1 g. (1 Mol.) Isosakuranetin mit 0.35 ccm. (10 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin in kleinem Proberöhrchen, so lösen sich die Krystalle von Isosakuranetin allmählich auf und es entsteht in 5 bis 6 Minuten eine klare Lösung. Dann wird diese Lösung mit Wasser versetzt, die abgeschiedene Acetyl-verbindung abfiltriert und aus 80–90-proz. Alkohol umkrystallisiert. Weisse Nadeln von Schmp. 173–175°C. In alkoholischer Lösung gibt die Substanz mit Ferrichlorid eine purpurbraune Reaktion und bei der Reduktion mit Mg und konz. Salzsäure zeigt sie eine kirschrote Färbung. Ausbeute 0.1 g.

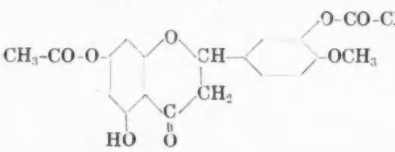


Gef.: C 59.32; H 5.44. Ber. für $C_{18}H_{16}O_6 \cdot 2H_2O$: C 59.34; H 5.53%.

8. Isosakuranetin-5,7-diacetat, $C_{20}H_{18}O_7$. 0.1 g Isosakuranetin wird mit 0.35 ccm. Essigsäure-anhydrid (10 Mol.) und 2–3 Tropfen Pyridin versetzt und auf dem siedenden Wasserbade 30 Minuten lang erhitzt. Das Produkt wird aus 90-proz. Alkohol umgelöst und erwies sich als schwer krystallisierbar. Schliesslich schieden sich farblose Nadeln vom Schmp. 138–140°C. Sehr leicht löslich in Alkohol. Eisenchloridreaktion negativ. Farbreaktion bei der Reduktion mit Mg und konz. Salzsäure stark prositiv. Ausbeute ca. 0.05 g.

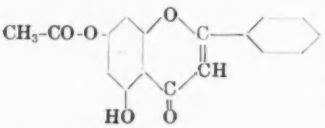
Gef.: C 59.09; H 5.25. Ber. für $C_{20}H_{18}O_7 \cdot 2H_2O$: C 59.11; H 5.46%.

9. Hesperetin-7.3′-diacetat, $C_{20}H_{18}O_8$. Versetzt man 0.2 g (1 Mol.) Hesperetin mit 0.7 ccm. (10 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin. so gehen die Krystalle von Hesperetin unter Wärmeentwicklung allmählich in Lösung innerhalb ca. 0.5–1 Minuten. Versetzt man diese Lösung mit Wasser, so entsteht schwer erstarrende harzige Masse. Diese Verbindung krystallisiert aus Alkohol in Nadeln oder prismatischen Krystallen vom Schmp. 103–105°C. Die alkoholische Lösung zeigt mit Ferrichlorid eine purpurbraune Färbung.



Gef.: C 62.00; H 5.03. Ber. für $C_{20}H_{18}O_8$: C 62.18; H 4.70%.

10. Chrysin-7-monoacetat, $C_{17}H_{12}O_5$. 0.15 g. Chrysin werden in einem kleinen Röhrchen mit 0.6 ccm. (10 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin gemischt und mit Glasstab umgerührt, so dass sich nach 1–1.5 Min. das Gemish verflüssigt und dann zu einer Krystallmasse erstarrt. Nach Ablauf weiterer 2–3 Minuten versetzt man die Reaktionsmasse mit Wasser. Die ausfallende Krystallmasse wird abgesaugt und aus 90-proz. Alkohol umkrystallisiert. Die so erhaltene Monoacetyl-verbindung schmilzt bei 160–165°C. Leicht löslich in heissem Alkohol. Die alkoholische Lösung gibt mit Ferrichlorid purpurbraune Färbung. Ausbeute ca. 0.15 g.



Gef.: C 69.20; H 3.99. Ber. für $C_{17}H_{12}O_5$: C 68.91; H 4.08%.

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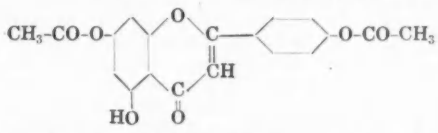
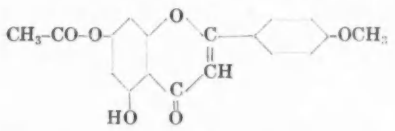
(34) G. Heller, *Ber.*, **45** (1912), 2389.

11. Apigenin-7.4′-diacetat, $C_{19}H_{14}O_7$. 0.1 g. Apigenin (1 Mol.) wird mit 0.4 ccm. (10 Mol.) Essigsäure-anhydrid und 2 Tropfen Pyridin versetzt. In ca. 3 Minuten ist die Reaktion beendigt. Schwache Wärmeentwicklung und Verflüssigung der Reaktionsmasse. Nach dem Versetzen mit Wasser wird die Acetylverbindung abgesaugt und aus 90-proz. Alkohol umkrystallisiert. Weisse Nadeln vom Schmp. 192–193°C. Purpurbraune Eisenchloridreaktion. Ausbeute ca. 0.1 g.

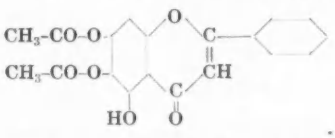


Gef.: C 64.47; H 3.96. Ber. für $C_{19}H_{14}O_7$: C 64.40; H 3.98%.

12. Acacetin-7-monoacetat, $C_{18}H_{14}O_6$. 0.1 g. (1 Mol.) Acacetin wird mit 0.35 ccm. (10 Mol.) Essigsänre-anhydrid uud 2 Tropfen Pyridin versetzt. Die Reaktion wird nach ca. 2–3 Minuten beendigt. Wie üblich mit Wasser versetzt und die abgeschiedene Krystalle aus 90-proz. Alkohol umkrystallisiert. Weisse kurze Nadeln vom Schmp. 203–208°C. Die alkoholische Lösung gibt mit Ferrichlorid eine purpurbraune Färbung. Ausbeute ca. 0.1 g.

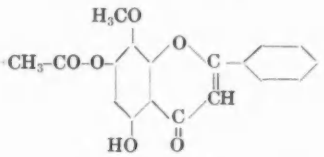


13. Baicalein-6.7-diacetat, $C_{19}H_{14}O_7$. 0.2 g. (1 Mol.) Baicalein werden mit 0.8 ccm. (10 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin versetzt und mit Glasstab vermischt. In 2–3 Minuten ist die Reaktion beendigt, mit Wasser versetzt und abfiltrierte Acetylverbindung aus 90-proz. Alkohol umkrystallisiert. Weisse Nadeln vom Schmp. 194°C. Die alkoholische Lösung zeigt mit Eisenchlorid eine purpurbraune Färbung. Leicht löslich in heissem Alkohol. Ausbeute ca. 0.2 g.



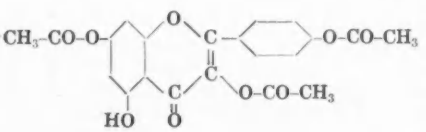
Gef.: C 64.34; H 3.91. Ber. für $C_{19}H_{14}O_7$: C 64.40; H 3.98%.

14. Wogonin-7-monoacetat, $C_{18}H_{14}O_6$. 0.15 g. Wogonin werden mit 0.55 ccm. (10 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin versetzt. Nach 1 Minuten Umrühren endet die Reaktion. Goldgelbe Wogoninkrystalle verwandelt sich zu schwach gelben Nadeln. Mit Wasser versetzt, abfiltriert, aus 90-proz. Alkohol umkrystallisiert, bildet das Acetylwogonin lange hellgelbe Nadeln vom Schmp. 159–161C°. Eisenchloridreaktion in alkoholischer Lösung purpurbraun (olivengrünlich). Ausbeute ca. 0.15 g.



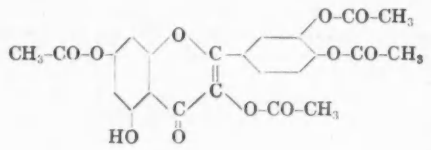
Gef.: C 66.37; H 4.37. Ber. für $C_{18}H_{14}O_6$: C 66.26; H 4.32%.

15. Kämpferol-3.7.4′-triacetat, $C_{21}H_{16}O_9$. Zur Gewinnung des Triacetyl-kämpferols werden 0.2 g. (1 Mol.) Kämpferol mit 0.7 ccm. (10 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin versetzt und mit Glasstab gut umgerührt. In 1.5 Minuten wird die Acetylierung vollendet. Die Reaktionsmasse wird dann mit Wasser versetzt, das Acetylderivat abgesaugt, mit Wasser gewaschen und aus 90-proz. Alkohol umkrystallisiert. Weisse Nadeln vom Schmp. 177°C. Leicht löslich in heissem Alkohol. aber schwer löslich in kaltem Alkohol. Eisenchloridreaktion purpurbraun. Ausbeute 0.2 g.



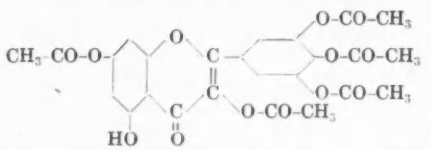
Gef.: C 61.40; H 4.14. Ber. für $C_{21}H_{16}O_9$: C 61.17; H 3.91%.

16. Quercetin-3.7.3.′4′-tetracetat, $C_{23}H_{18}O_{11}$. 0.3 g. (1 Mol.) lufttrocknes Quercetin werden in ein kleines Röhrchen von etwa 5 ccm Inhalt eingerführt, mit 1 ccm. (10 Mol.) Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt und mit Glasstab bei Zimmertemperatur umgerührt, wobei sich gelbe Krystalle von Quercetin nach und nach in weissen Nadeln von Acetylverbindung umwandeln. Unter Wärmetönung ist die Reaktion nach 4-5 Minuten beendigt. Nach 10 Minuten Stehenlassen wird die Reaktionsmasse mit Wasser gewaschen und aus 90-proz. Alkohol umkrystallisiert. Farblose Nadeln. Das Teteracetylderivat schmilzt bei 160-162° und zeigt in alkoholischer Lösung mit Ferrichlorid eine purpurbraune Färbung. Ausbeute etwa 0.3 g.



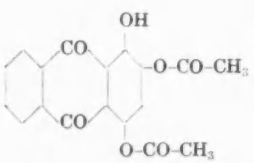
Gef.: C 58.73; H 4.05. Ber. für $C_{23}H_{18}O_{11}$: C 58.70; H 3.86%.

17. Myricetin-3.7.3′.4′.5′-pentacetat, $C_{25}H_{20}O_{13}$. 0.2 g. Myricetin werden mit 0.65 ccm. (10 Mol.) Essigsäureanhybrid und 2-3 Tropfen Pyridin versetzt. In ca. 1 Min. verflüssigt sich das Gemisch, nach einer weiteren Minuten Umrühren beginnt die Reaktion unter schwacher Wärmeentwicklung und Erstarrung der Reaktionsmasse. Aus 90-proz. Alkohol scheidet sich das Acetat in langen Nadeln vom Schmp. 189-190°C. ab. Schwer löslich in kaltem, aber leicht löslich in heissem Alkohol. Eisenchloridreaktion purpurbraun. Ausbeute ca. 0.2 g.



Gef.: C 57.23; H 3.81. Ber. für $C_{25}H_{20}O_{13}$: C 56.84; H 3.82%.

18. Purpurin-2.4-diacetat, $C_{18}H_{12}O_7$. 0.2 g. (1 Mol.) Purpurin werden mit 0.8 ccm. (10 Mol.) Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt. Nach ca. 1 Min. Umrühren mit Glasstab beginnt die Reaktion und nach 5-6 Minuten bleibt kein rotes Purpurinkryställchen mehr. Die orangegelbe Reaktionsmasse wird mit Wasser versetzt, abfiltriert und aus 90-proz. Alkohol umkrystallisiert. Orangegelbe Krystalle vom Schmp. 175-178°C. In alkoholischer Lösung zeigt die Acetylverbindung eine jodbraune Eisenchloridreaktion. Ausbeute ca. 0.2 g.



Gef.: C 63.29; H 3.52. Ber. für $C_{18}H_{12}O_7$: C 63.53; H 3.56%.

19. Salicylsäure-acetat, $C_6H_4(O\cdot CO\cdot CH_3)\cdot COOH^{1,2}$. 0.5 g. Salicylsäure werden mit 1.85 ccm. (5 Mol.) Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt, wodurch bald klare Lösung entsteht. Versetzt man diese Lösung mit Wasser, so entsteht schwer erstarrende ölige Masse. Das Produkt erstarrt, bald krystallinisch und wird aus verd. Alkohol umkrystallisiert. Farblose Nadeln oder Prismen vom Schmp. 134-135°C. Eisenchloridreaktion völlig negativ.

20. Brenzcatechin-*o*-carbonsäure-diacetat, $C_6H_3(O\cdot CO\cdot CH_3)_2\cdot COOH^{1,2,3}$. 0.2 g. Brenzcatechin-*o*-carbonsäure werden mit 0.66 ccm. (5 Mol.) Essigsäere-anhydrid und 2-3 Tropfen Pyridin versetzt. In ca. 1-2 Min. entsteht klare Lösung. Versetzt man diese Lösung mit Wasser, so entsteht schwer erstarrende ölige Masse. Diese Verbindung krystallisiert aus verd. Alkohol in farblosen Nadeln vom Schmp. 146-170°C. Eisenchloridreaktion ganz negativ.

21. β-Resorcylsäure-diacetat, $C_6H_3(O\cdot CO\cdot CH_3)_2\cdot COOH^{1,2,3}$. 0.2 g. β-Resorcylsäure werden mit 0.66 ccm. Essigsäure-anhydrid und 2-3 Tropfen Pyridin versetzt. In ca. 1-2 Min. entsteht klare Lösung. Beim Versetzen mit Wasser entsteht öliges Reaktionsprodukt, welches im Kühlraum bald krystallinisch erstarrt und aus wenigem Alkohol in

prismatischen Nadeln krystallisiert. Die alkoholische Lösung zeigt mit Ferrichlorid keine Färbung. Schmp. 136–137°C.

22. **Pyrogallol-o-carbonsäure-triacetat,** $C_6H_2(O\cdot CO\cdot CH_3)_3\cdot COOH^{1,2,3,4}$. Die Herstellung des Triacetats erfolgt durch unmittelbares Zusammenbringen von Pyrogallol-o-carbonsäure (0.2 g.) mit 0.6 ccm. (5 Mol.) Essigsäure-anhydrid und 2–3 Tropfen Pyridin. In ca. 1 Min. entsteht braune Lösung unter Temperaturerhöhung. Diese Verbindung krystallisiert aus verd. Alkohol in farblosen Nadeln vom Schmp. 163–164°. Prismatische Nadeln aus Xylol[33]. In alkoholischer Lösung gibt die Substanz mit Eisenchlorid keine Färbung.

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A Note to the Paper "On the Metallo-organic Compounds. X. Electroisomerism in the Triethyltin Group."

By Taichi HARADA.

(Received July 4, 1941.)

In the paper "on the metallo-organic compounds. X. Electroisomerism in the triethyltin group,"[1] the author reported a difference between the rates of oxidation of two preparations of the triethyltin group in a polymerized form prepared in liquid ammonia by the following two methods:

$$\text{A I.} \quad 2(C_2H_5)_3SnX + 2Na = ((C_2H_5)_3Sn)_2 + 2NaX \quad (X = \text{halogen})$$

$$\text{II.} \quad ((C_2H_5)_2SnNa)_2 + 2C_2H_5X = ((C_2H_5)_2SnC_2H_5)_2 + 2NaX$$

Kraus and Greer[2] also observed that a similar behavior exists between the following two dimethyltin preparations:

$$\text{B I.} \quad (CH_3)_2SnX_2 + 2Na = (CH_3)_2Sn + 2NaX$$

$$\text{II.} \quad (CH_3)_2SnNa_2 + (CH_3)_2SnX_2 = ((CH_3)_2Sn)_2 + 2NaX$$

that is, the latter (B II) preparation is much more sensitive to oxygen than that of the former (B I). In accounting for the difference between the rates of oxidation of the preparations (A I) and (A II), the present author believed that an explanation may be found by assuming the cause to be due to the method of preparation or the difference in their electronic constitutions (electroisomers). However, such assumption must now be withdrawn since it is not only hasty but is inconceivable that the triethyltin group can exist in two isomeric forms with present knowledge. The different rates of oxidation in question can not be explained satisfactorily at present but it may be correct to assume that the difference might be due to some contaminating trace of impurity in the preparation. Further investigation on this point was not carried out because it is not within the scope of this original investigation.[3]

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(1) T. Harada, this Bulletin, **15** (1940), 481.
(2) Kraus and Greer, *J. Am. Chem. Soc.*, **47** (1925), 2568.
(3) Kraus and T. Harada, *ibid.*, **47** (1925), 2416; T. Harada, *Sc. Pap. I. P. C. R.*, **38** (1940), 146.